innovative block resistance additives: a sustainable solution to PFAS in coatings

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presentation overview

1. understanding block resistance
2. exploring materials and additives for block resistance
3. phosphate ester compositions
4. Ashland phosphate ester for block resistance
5. surfactant characterization (HLB vs HLD)
6. surface tension measurements
7. Langmuir trough analysis of surfactant packing

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Why is block resistance important?

- areas where painted surfaces contact can lead to blocking damage
  - doors
  - windows
  - cabinets
  - drawers
- efficiency issue in manufacturing and construction
  - early and high temperature block resistance is necessary

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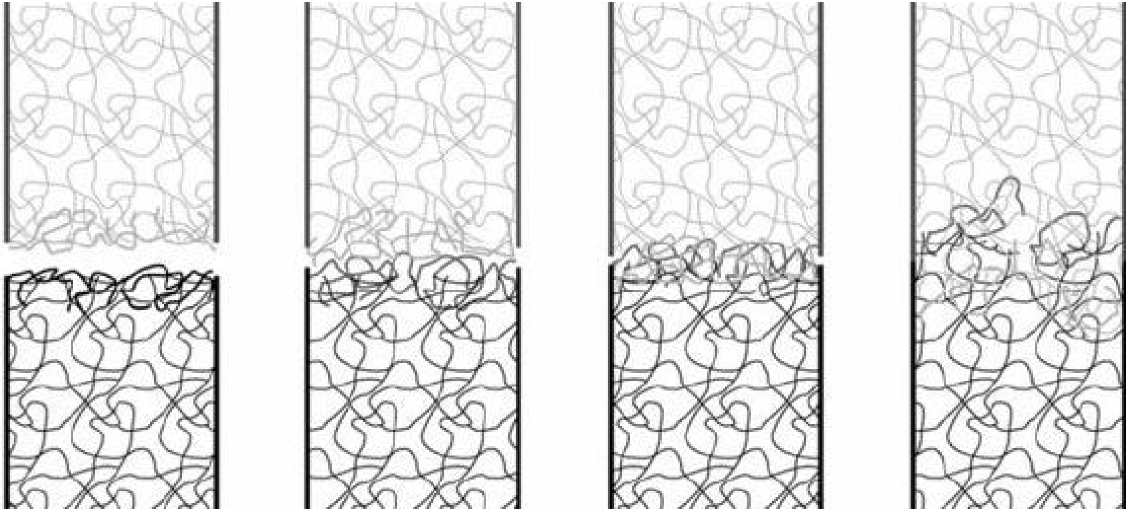
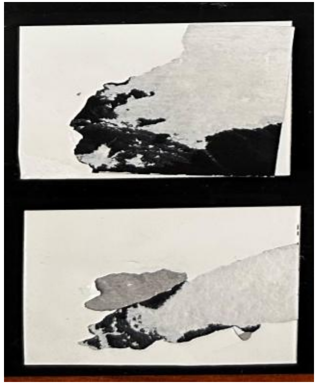
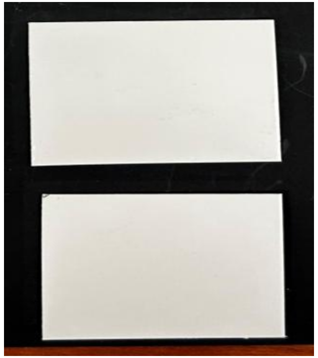
What causes blocking?

slow curing/coalescence and low Tg can lead to blocking
polymers remaining amorphous remain semi-mobile
diffusion of polymer chains across the interface





poor block resistance



good block resistance

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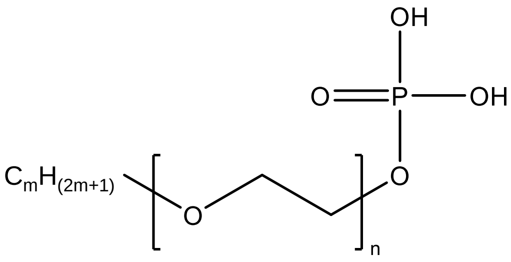
materials commonly used for block resistance

- per or poly fluorinated alkyl substances (PFAS)
  - PFAS dramatically reduce surface energy making it harder for two painted surfaces to adhere to each other
- phosphate esters (for block resistance)
  - migrate to film surface and orient to create hydrophobic alkyl layer between paint surfaces
- silicone
  - organomodified silicones and polysiloxanes reduce surface energy and enhance slip
- waxes
  - polyethylene (PE) or polypropylene (PP) waxes migrate to the film surface during drying, creating a low-energy layer

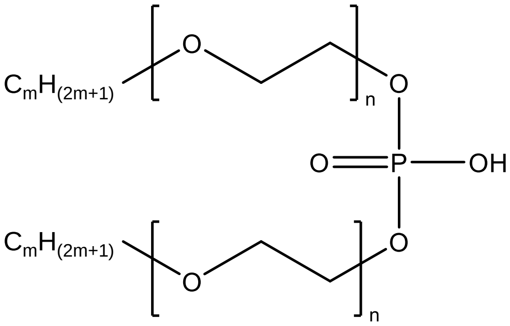
phosphate ester surfactants

formed by esterification reaction with phosphate and alcohol

- mono-to-diester ratio affects hydrophilic/hydrophobic character
  - monoesters: compatibility
  - diesters: wetting & emulsification
- degree of ethoxylation of alcohol: hydrophilic character, water solubility
- hydrophobe (fatty alcohols): chain length, linear or branched
- coesters: combining different alcohols & ethoxylated alcohols
- solubility of phosphate esters changes with pH



monoester



diester

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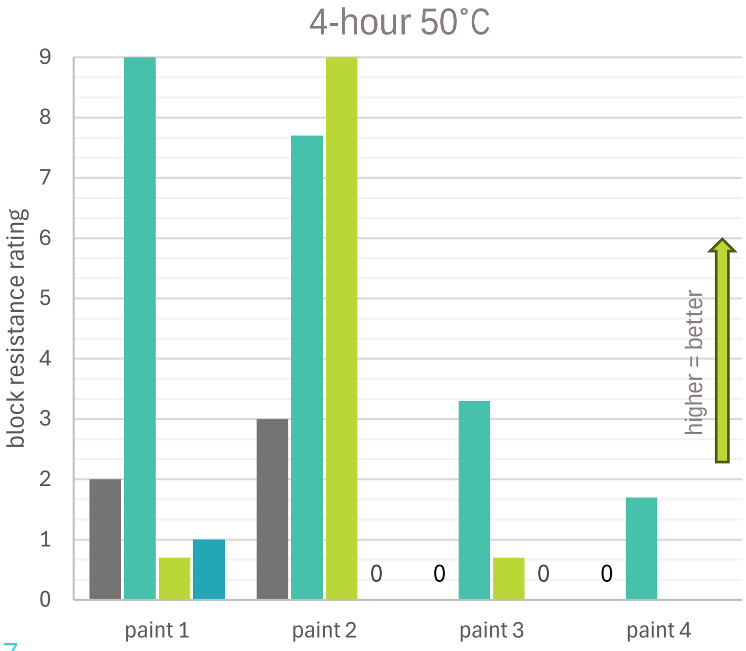
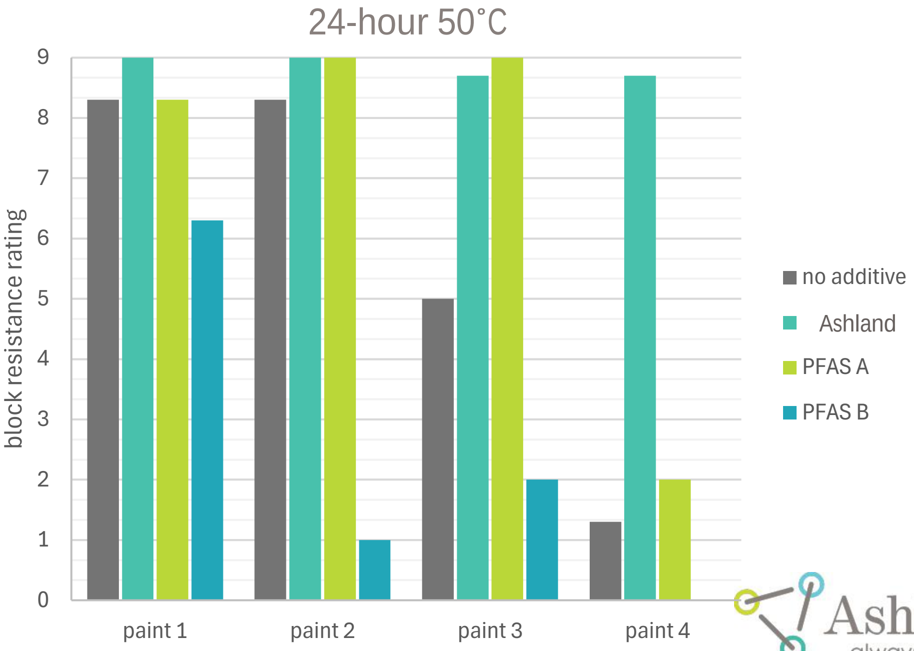
high temperature block

Ashland block additive alternative to PFAS for block resistance

tested in 4 latex paints for early (4-hour) and 24-hour block resistance at 50˚C





waterborne latex paints dosed at 0.3 wt% additive

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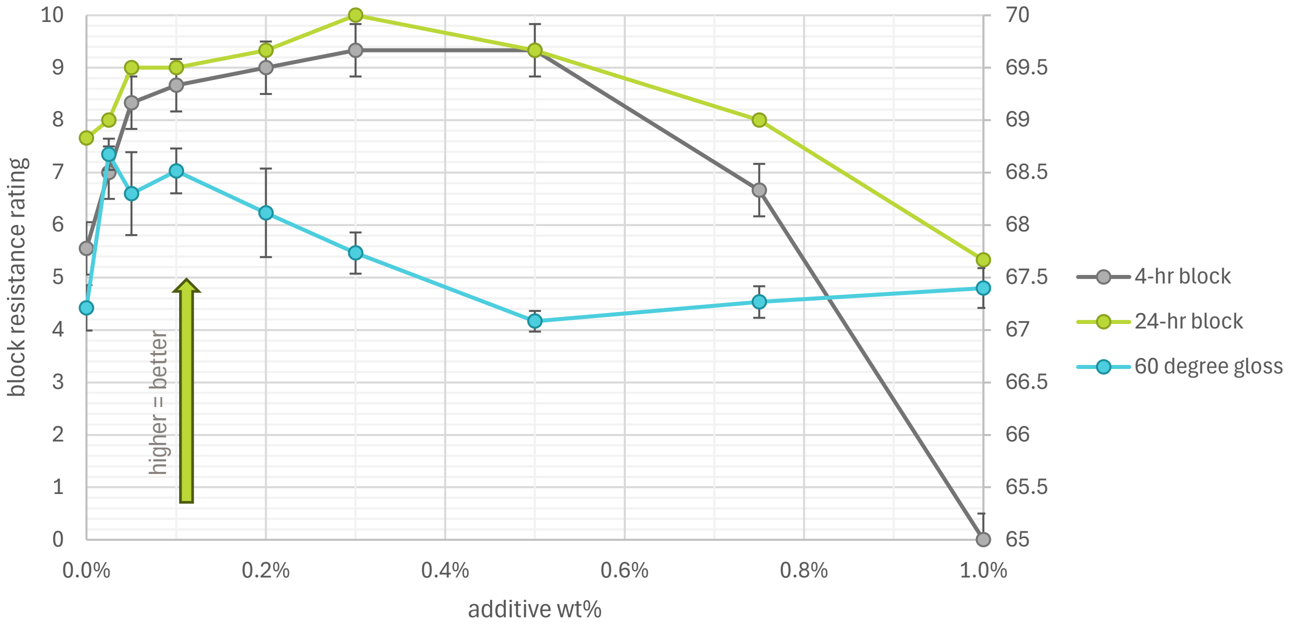
product dosing for block



a dose ladder should be conducted when formulating with block additives

overdosing causes loss of block resistance!

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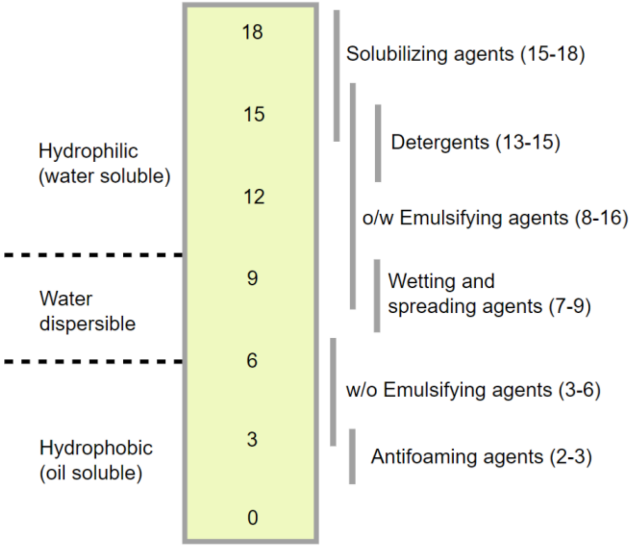
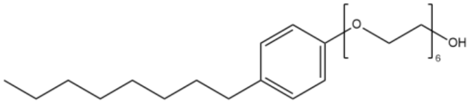
hydrophilic / lipophilic balance (HLB) nonionic surfactants

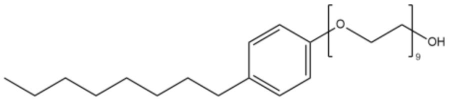
- calculated balance of hydrophilic and lipophilic molecule components
- frequently used to select nonionic surfactant
- number (0 – 20) indicates emulsification ability / water solubility
- limitations to reliability and scope



$$HLB = (Mw_{hydrophilic} / Mw_{total}) * 20$$



nonylphenol 6 mol ethoxylate HLB = 10.9



nonylphenol 9 mol ethoxylate HLB = 12.9

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limitations of HLB

- only reliable for linear ethoxylate surfactants (NONIONICS ONLY)
  - can be estimated empirically for other architecture
- HLB is a single number for a surfactant (no salt, pH, or Temp.)
  - the balance is between surfactant and oil
    - an oil needs to be matched to the needed HLB
- cannot differentiate structural effects of similar HLB surfactants

> As Stubenrauch likes to point out in lectures[7], the HLB of C8E4, C10E5 and C12E6 are all ~12.5 but their CMC values change from 8.6e-3 to 8.0e-5. And of course the solubilizing power of a shorter C8 and E4 chains is less than that of a longer C12 and E6 chains, so irrespective of CMC the C12 is generally a more effective surfactant.

Surfactant Science Principles and Practice by Prof. Steven Abbott

useful for basic ethoxylate surfactants paired with well studied oils at room temperature with no salts

hydrophilic / lipophilic *difference* (HLD) any surfactant (50:50 WOR)

Salager, Aubry, Sabatini, Abbott et al.

$$HLD = SurfNo + OilNo + f(T) + f(S)$$
$$HLD = Cc - k.EACN - \alpha.\Delta T + f(S)$$

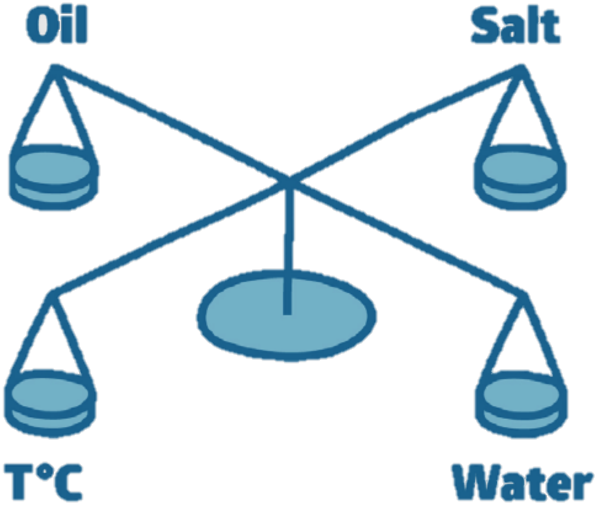
nonionic surfactants:

$$HLD = C_c - 0.17(EACN) + 0.06(T - 25) + 0.13(S)$$

ionic surfactants:

$$HLD = C_c - 0.17(EACN) - 0.01(T - 25) + ln(S)$$

- C_c = surfactant characteristic curvature (HLB analogue)
- EACN = oil equivalent alkane carbon number
- S = g NaCl / 100mL
  - S=(58/Mw)g/100mL for other monovalent salts
  - di, tri-valent salts must account for ionic strength



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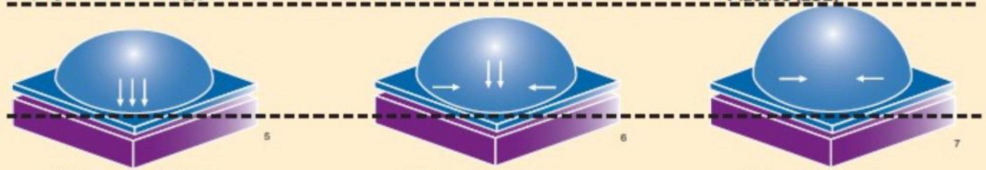
wetting behavior driven by surface tension

$$-\frac{\Delta G_w}{a} = \gamma_{SA} - (\gamma_{SL} + \gamma_{LA}) = S_{L/S}$$

surface tension of the liquid

$$\cos(\theta) = (\gamma_{SA} - \gamma_{SL})/\gamma_{LA}$$



Metal Surfaces (High Surface Energy)

mJ/m²	Surfaces
1103	Copper
840	Aluminum
753	Zinc
526	Tin
458	Lead
700-1100	Stainless Steel
250-500	Glass Porcelain

High Surface Energy Plastics (HSE)

mJ/m²	Surfaces
50	Kapton® Industrial Film
47	Phenolic
46	Nylon
45	Alkyd Enamel
43	Polyester
43	Epoxy Paint
43	Polyurethane Paint
42	ABS
42	Polycarbonate
39	PVC Rigid
38	Noryl® Resin
38	Acrylic

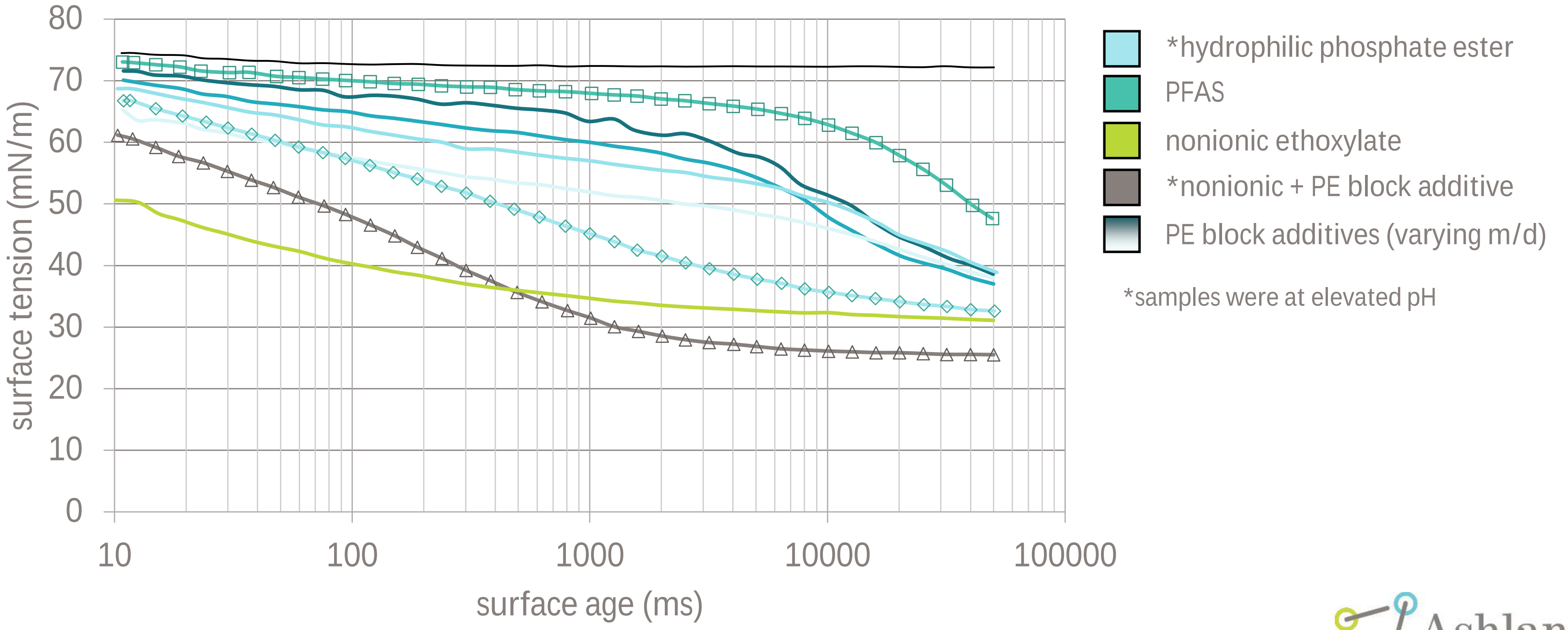
Low Surface Energy Plastics (LSE)

mJ/m²	Surfaces
37	PVA
36	Polystyrene
36	Acetal
33	EVA
31	Polyethylene
29	Polypropylene
28	Tedlar® Polyvinyl Fluoride Film
18	PTFE
*	Powder Coated Paints

$S_{L/S}$ = spreading coefficient

- when positive, surface free energy is reduced and spreading occurs

surface tension (dynamic)



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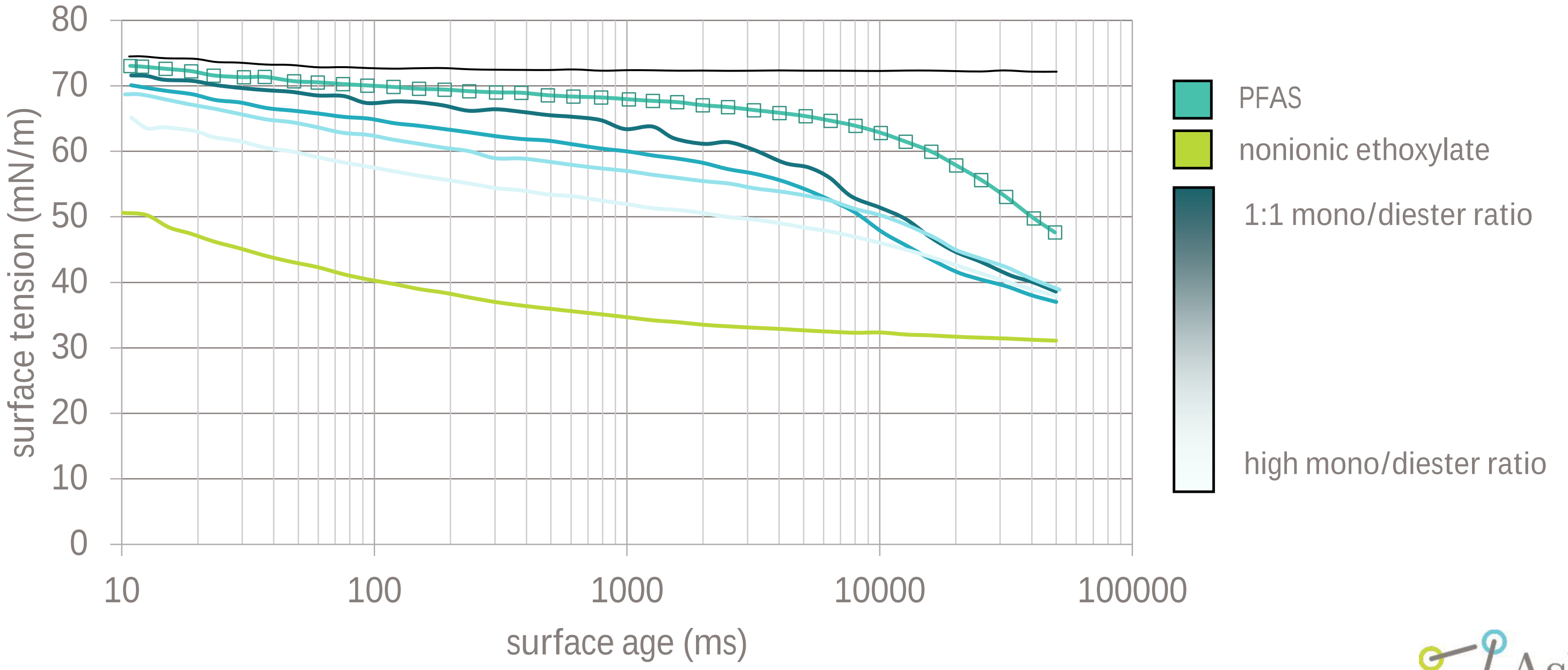
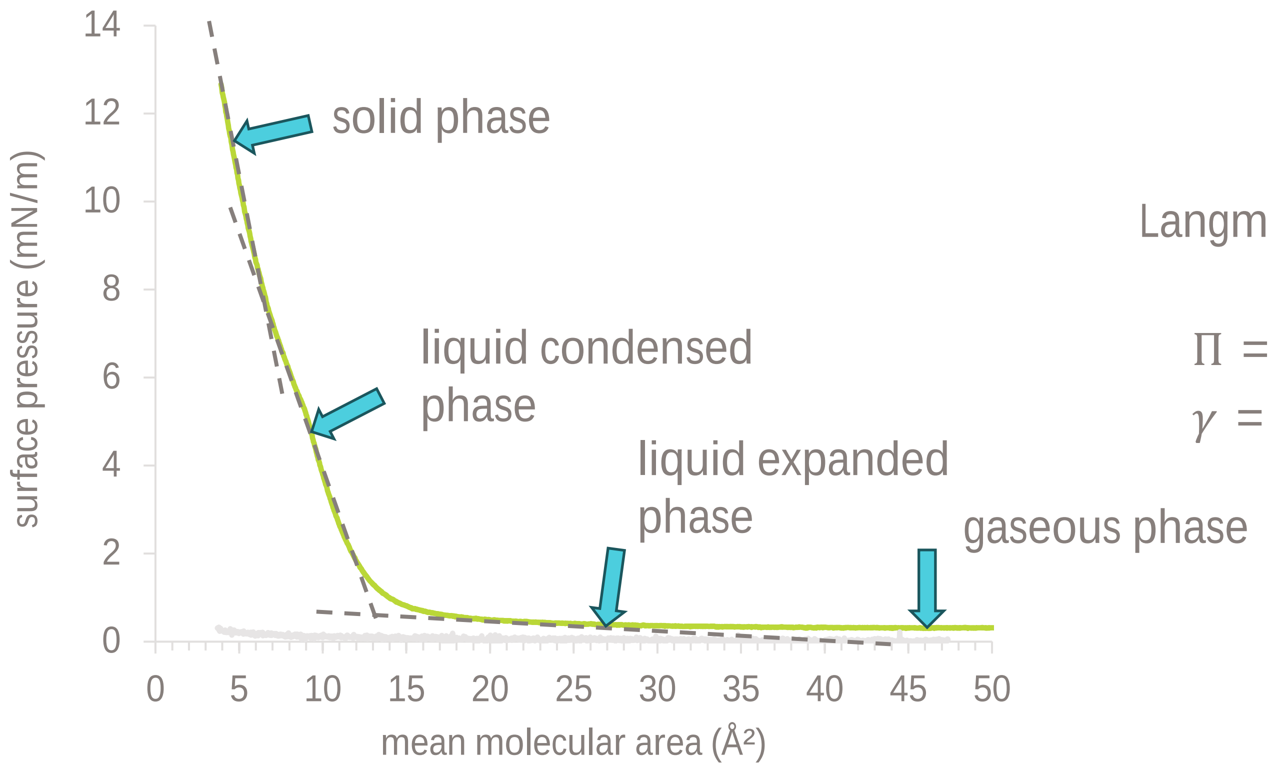
surface tension (dynamic)



Langmuir trough analysis



Langmuir trough

$$\Pi = \gamma_0 - \gamma$$

$$\gamma = 72 - \Pi$$

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Langmuir trough terminology

- Molecular Packing: shape and position of the isotherm reveal how the molecules pack together under confinement
- Phase Transitions: distinct regions and changes in slope indicate transitions between different physical phases of the monolayer
- Mean Molecular Area (MMA): point at which the monolayer transitions from the liquid condensed to the solid phase gives an estimate of the average area occupied by each molecule in the tightly packed monolayer
- Compressibility: slope indicates the compressibility of the monolayer, steeper slopes mean lower compressibility

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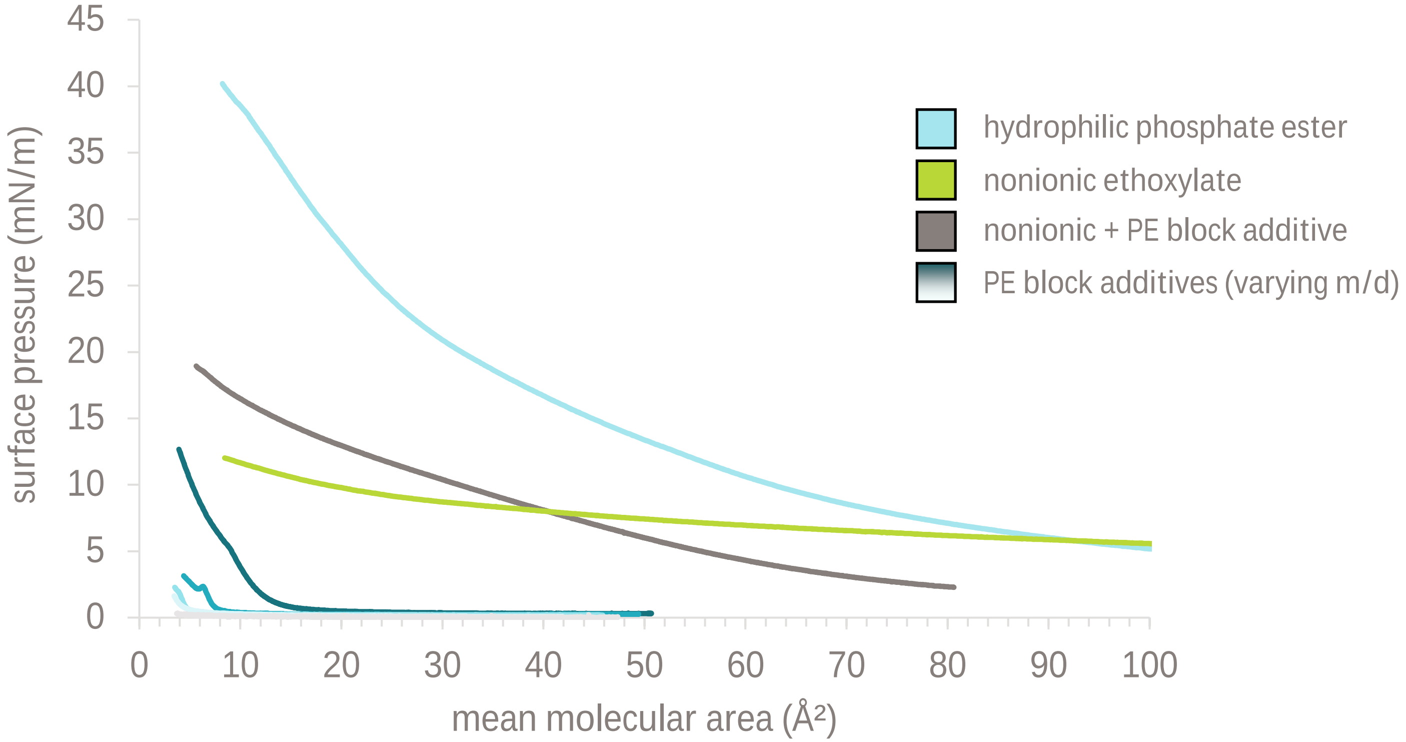
Langmuir trough of various surfactants



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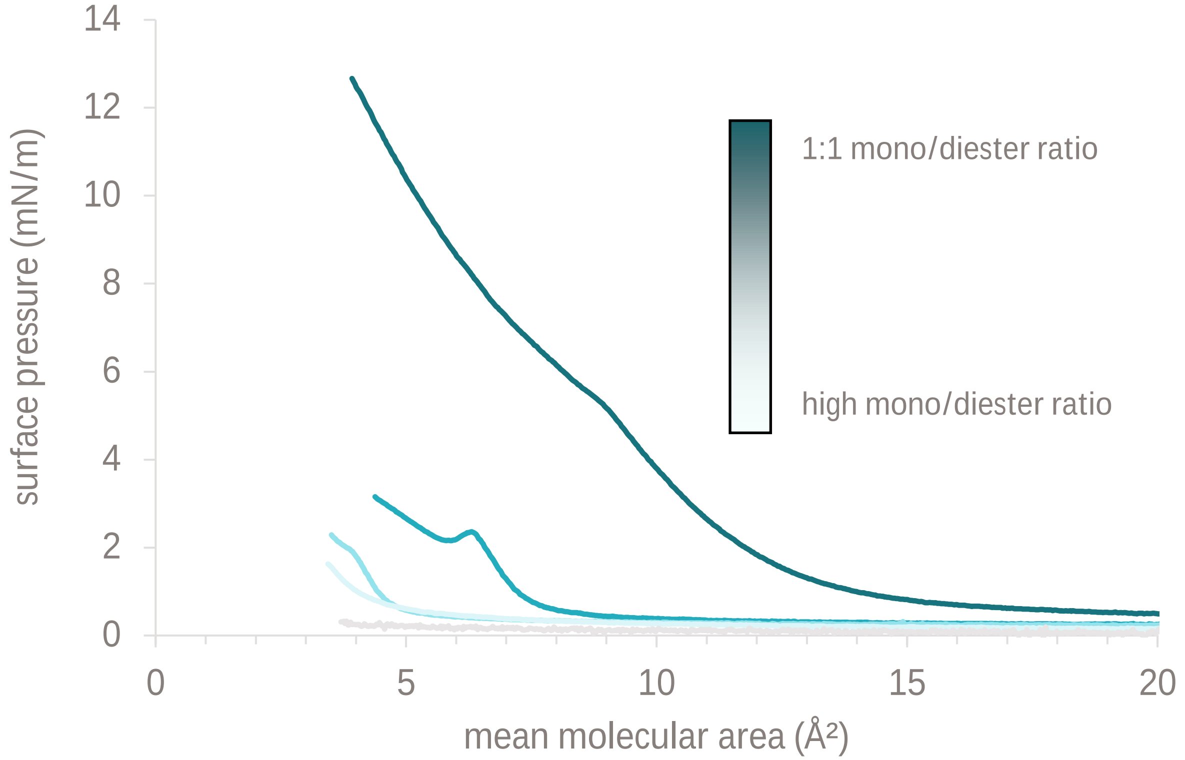
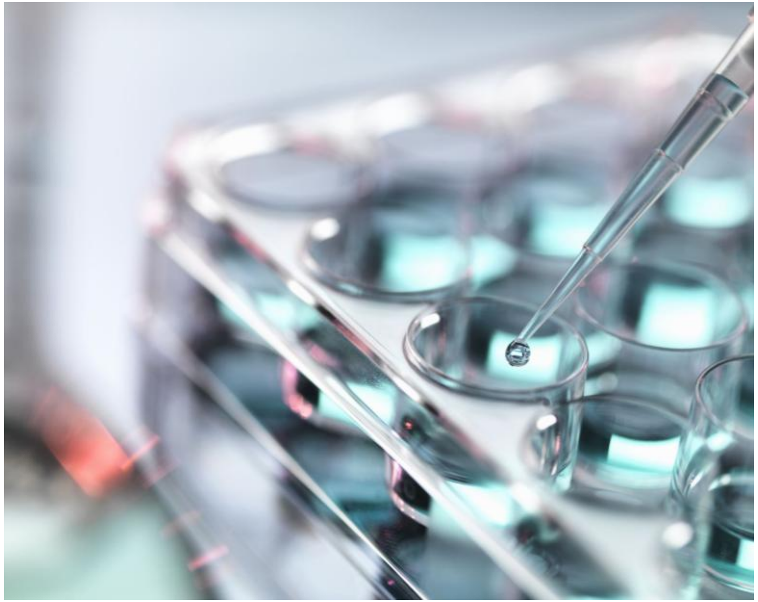
Langmuir trough of phosphate ester block additives



Ashland can optimize phosphate ester structure to maximize surfactant packing

improved molecular packing can lead to improved block resistance

conclusion: advancing sustainable block additives



- innovative additives offer effective PFAS alternatives for block resistance
- proper dosing is critical to maintain performance without overdosing
- understanding surfactant chemistry aids in optimizing additive performance
- improvements in molecular packing can lead to better block resistance
- ongoing research supports sustainable and efficient coating applications

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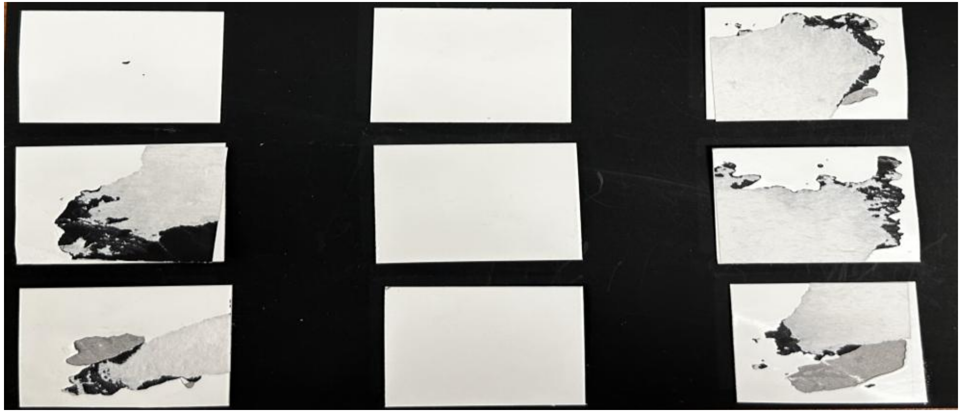
block testing rating system ASTM D4946

Peel Block Ratings	
10	**No tack**
9	**Trace tack**
8	**Very slight tack**
7	**Very slight – slight tack**
6	**Slight tack**
5	Moderate tack
4	Very tacky, no seal
3	5-25% seal
2	25-50% seal
1	50-75% seal
0	75-100% seal



Tack: the noise produced upon separation of blocked surfaces.
Seal: the physical damage to a paint film caused by the separation of blocked surfaces.

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surface tension (static & CMC)

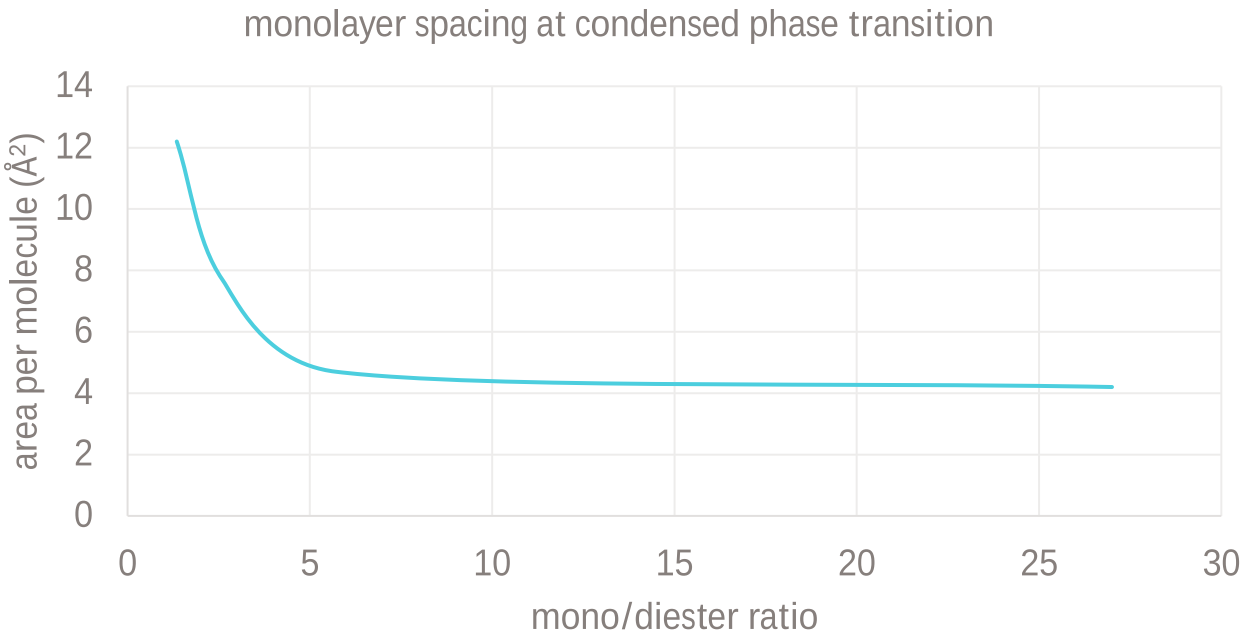
- 0.1 wt% actives

material	surface tension (mN/m)	CMC (mg/L)
PFAS	17.1	
hydrophilic phosphate ester	28.6	9
PE block additive high monoester	25.6	
PE block additive + nonionic	29.3	

Surface Pressure Measurements in DI water on a Langmuir Trough

1. gaseous phase: high molecular area, surface pressure near zero indicating no interactions
2. liquid expanded phase: molecules start to interact and gives gradual increase of surface pressure
3. liquid condensed phase: further compression leads to more significant increase in surface pressure
4. solid phase: steep rise in surface pressure indicates the formation of a highly ordered solid-like monolayer
5. collapse point: monolayer eventually cannot withstand the compression and collapses to multilayers or micelles

phosphate ester composition affect on molecular packing



≥ 6 mono to 1 diester, molecular packing is no longer affected