Controlling the Air/Liquid Interfaces

Presented at the 2023 CTT

Air/Liquid Interfaces in Organic Coatings

- Foam air/liquid/bubble/liquid/air
- Bubbles or air entrapment liquid/bubble/liquid
- Film surface air/liquid

Foam

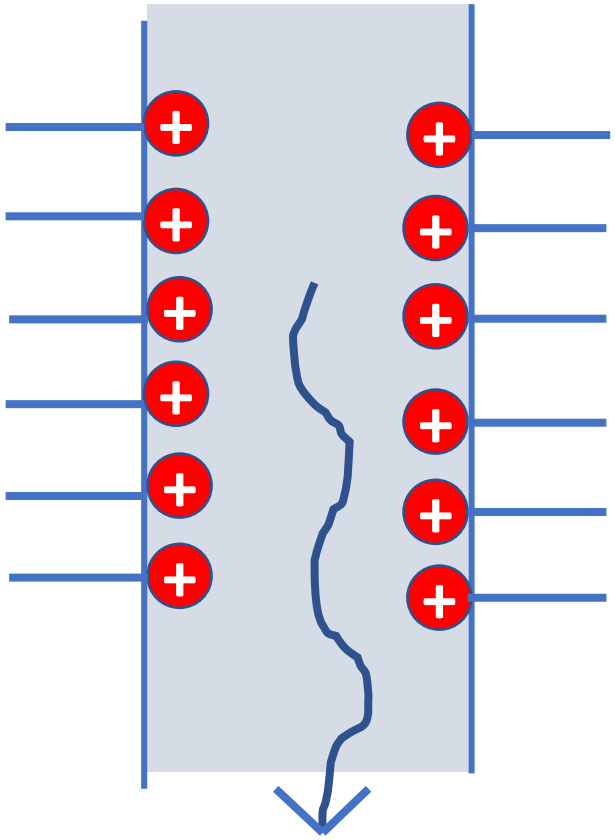
- Paint plants are not a foam friendly environments
- Foams do not pump, flow, etc.
- Foams do not transfer energy efficiently
- Foamed fluids do not meet packing weights
- Foam in coatings create film defects
- Foam degrades coatings ability to protect

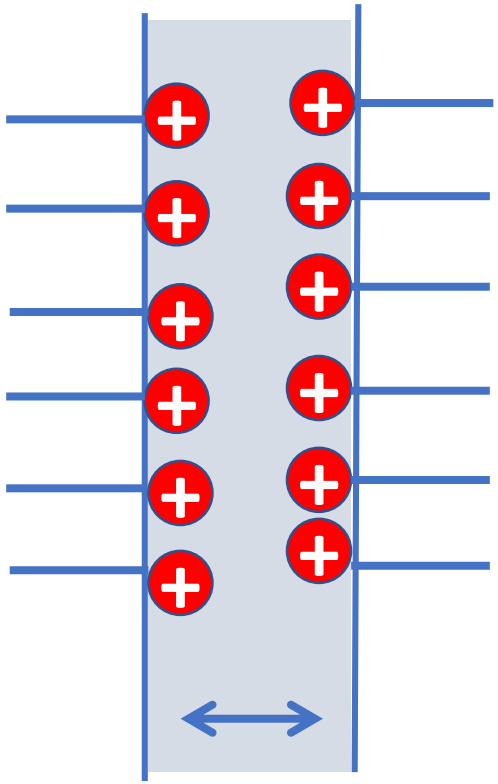
Conditions that create foam

- Introduction of a gas into the liquid
- Bubbles in liquids obey Stoke's Law
- Pure liquids do not form stable foam
- Presence of a soluble surface active agent
  - Displaced air
  - Entrapped air

$$V \sim \frac{r^2}{\eta}$$

Electrostatic Repulsion



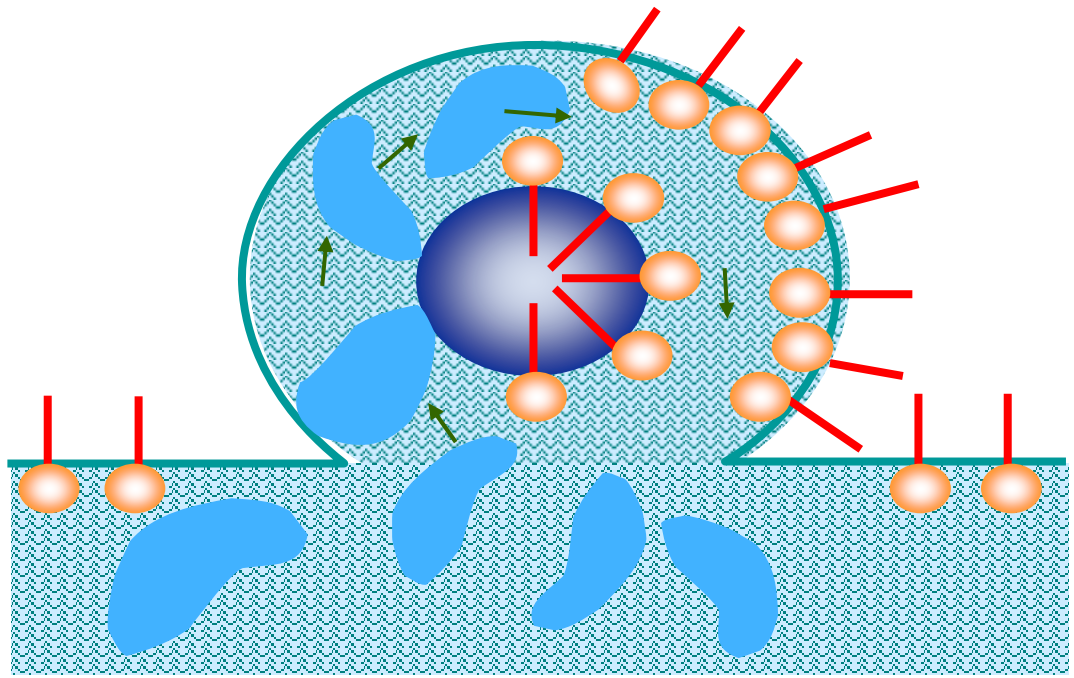


> 10 nm

Properties for Defoamers

- Insoluble in continueous phase
- Incompatible with the system
- Positive Entering Coefficient
- Positive Spreading Coefficient

Defoamers - Mechanisms

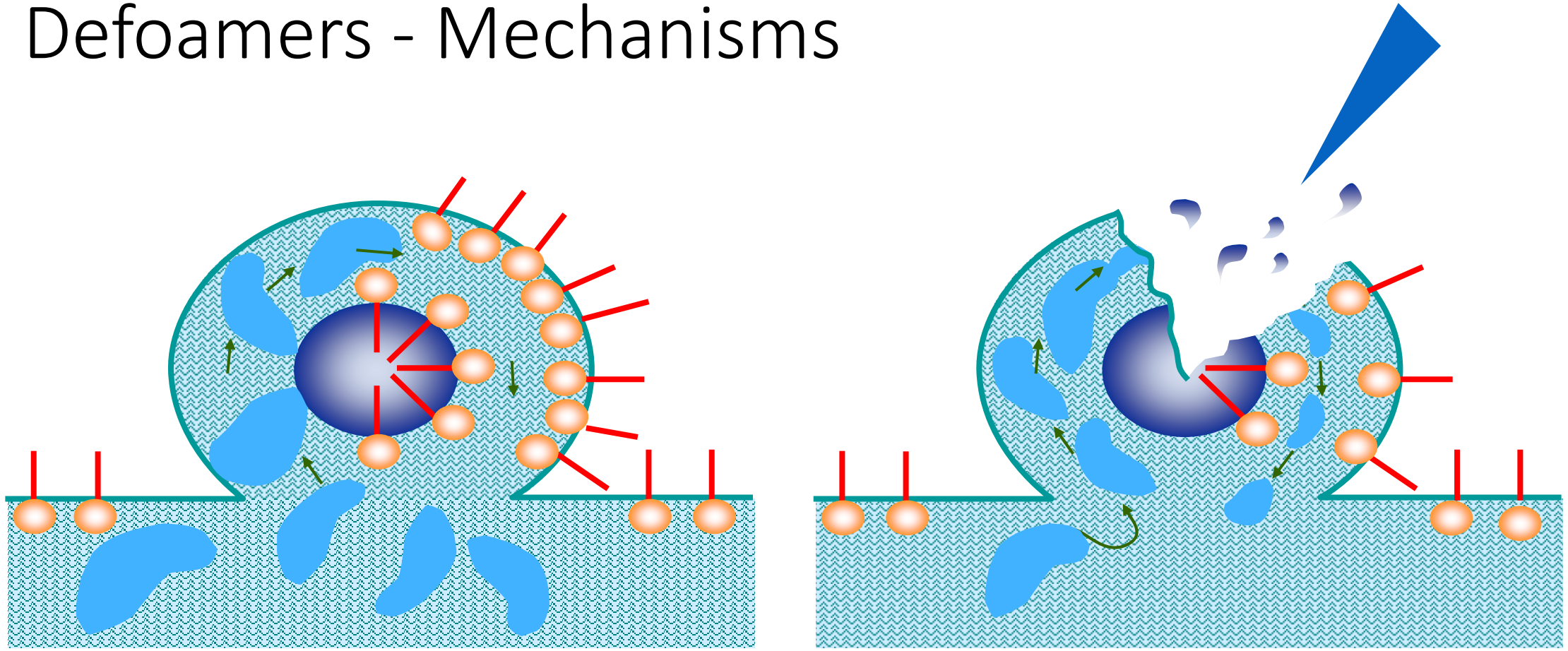


Positive spreading and entering coefficients drives defoamer into lamella

Displacing surfactants to make lamella unstable

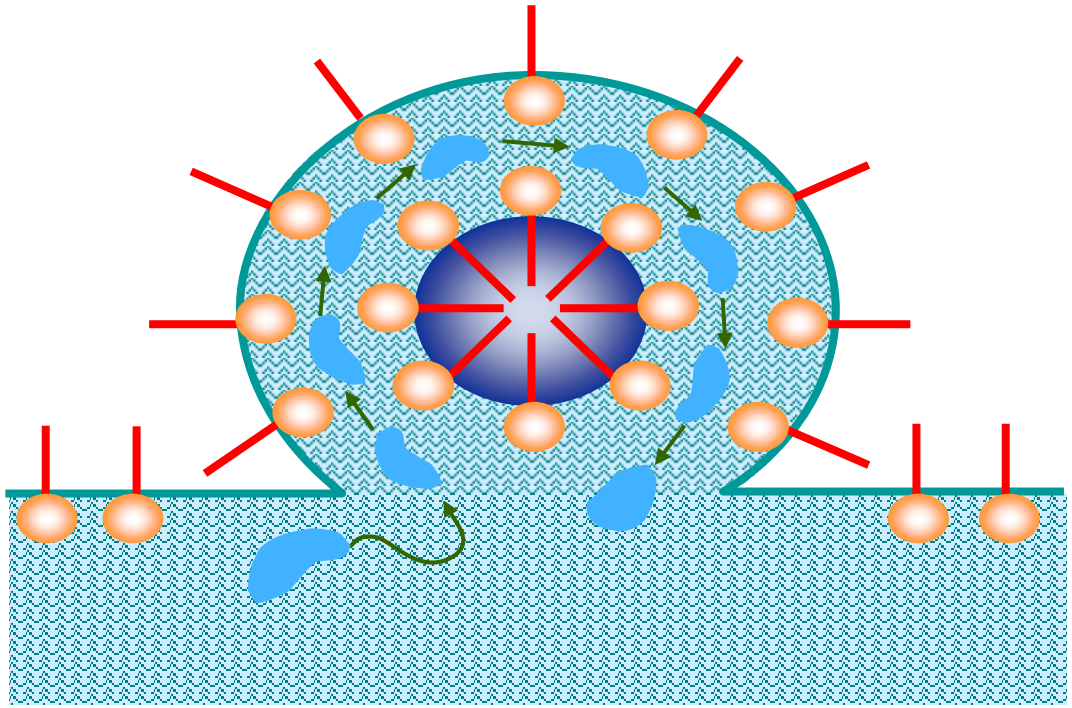
Function is dependent on particle size and chemistry

Defoamers - Mechanisms



Unstable lamella collapse = defoaming

Defoamers - Mechanisms



Shear reduces the defoamer particle size

No longer large enough to displace surfactant

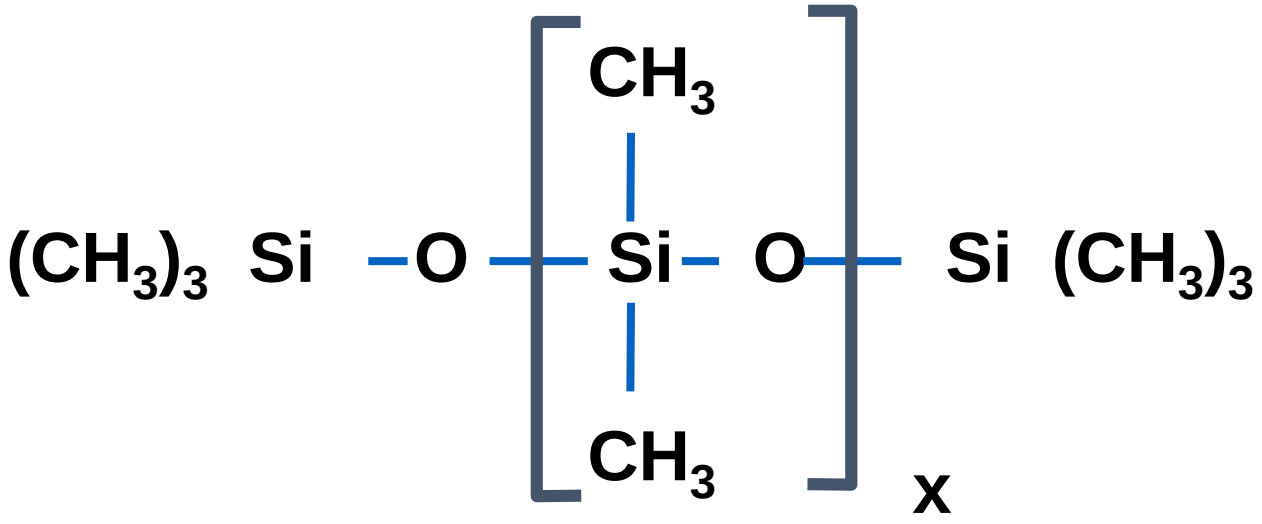
Insufficient material movement to destabilize lamella

Function is dependent on particle size and chemistry

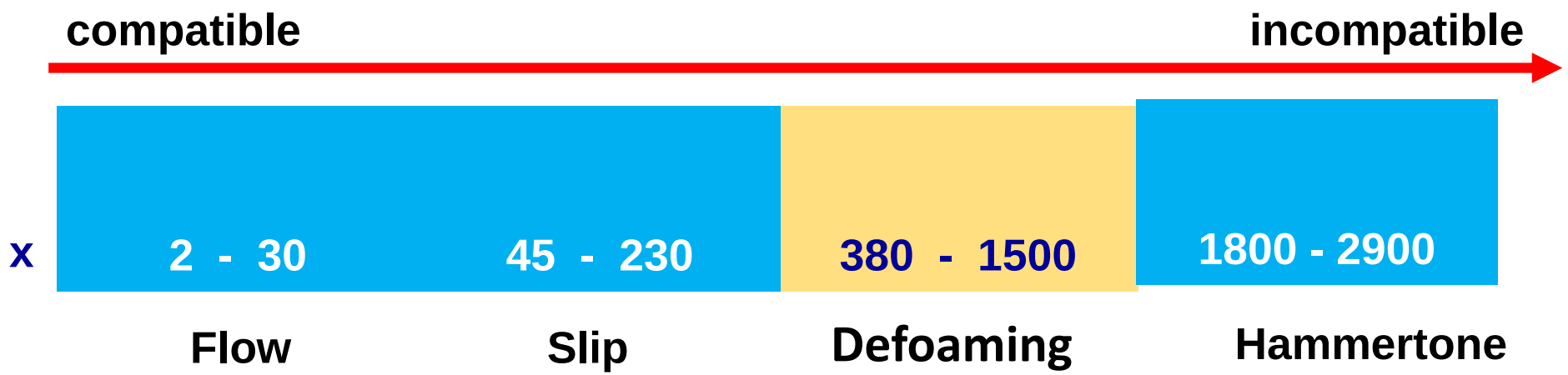
Typical Defoamer Contents

Mineral Oil	Polysiloxane	Polymeric
Mineral Oil Dispersant Hydrophobe PDMS	Modified PDMS Hydrophobe Fluoro mod	Acrylate Polyester Hydrophobe

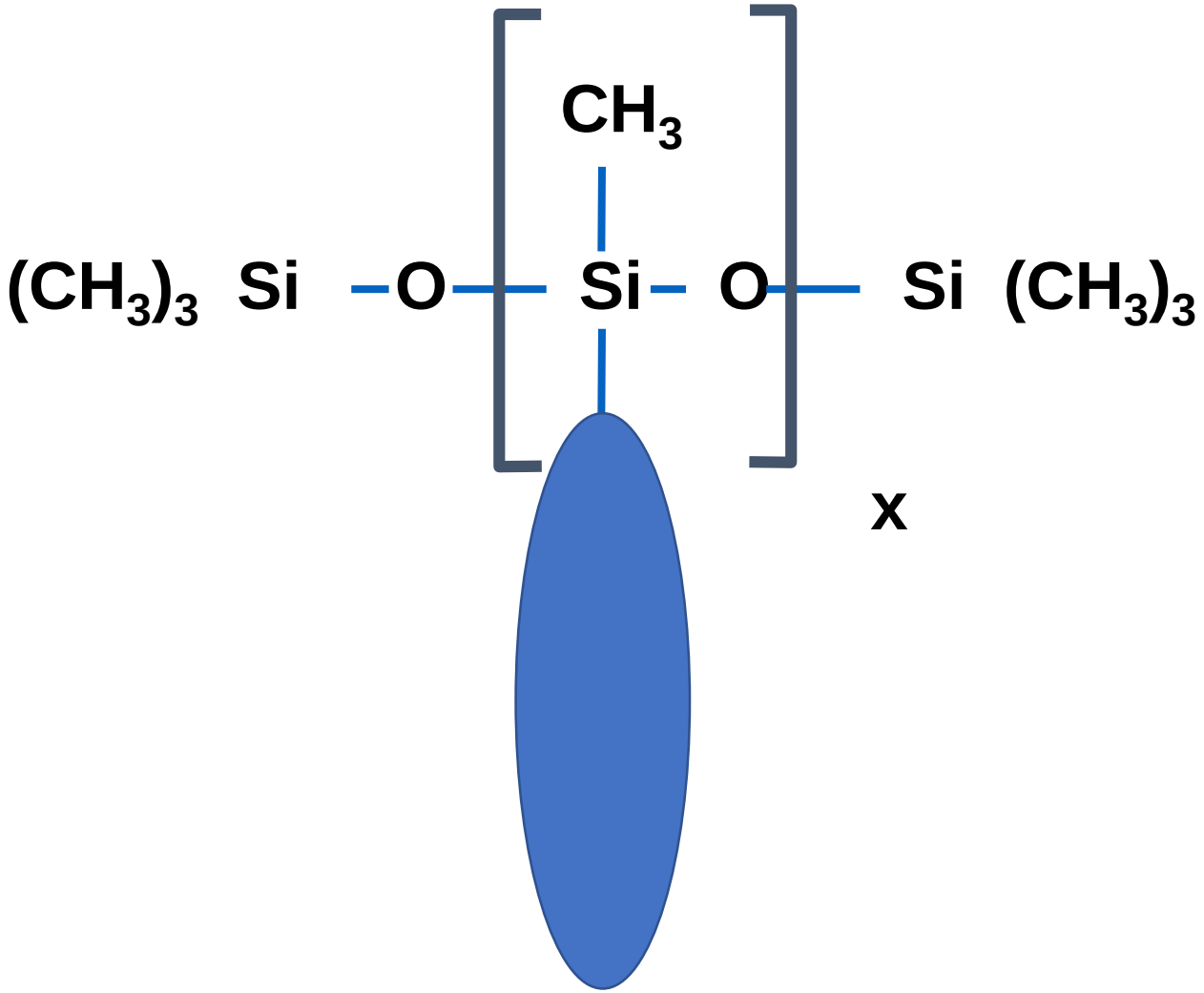
Unmodified PDMS



Silicone Oils



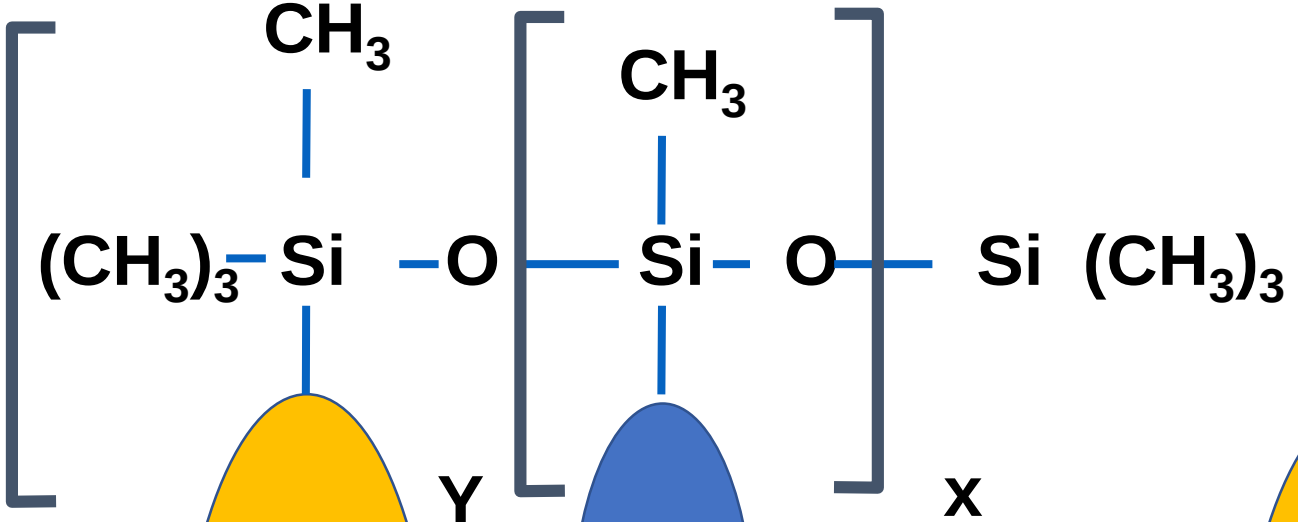
PDMS Modifications



CH_3	21
CH_2CH_3	26
$(CH_2)_9CH_3$	32

PDMS activity
is parameter
of alkyl chain length

PDMS Modifications



Activity

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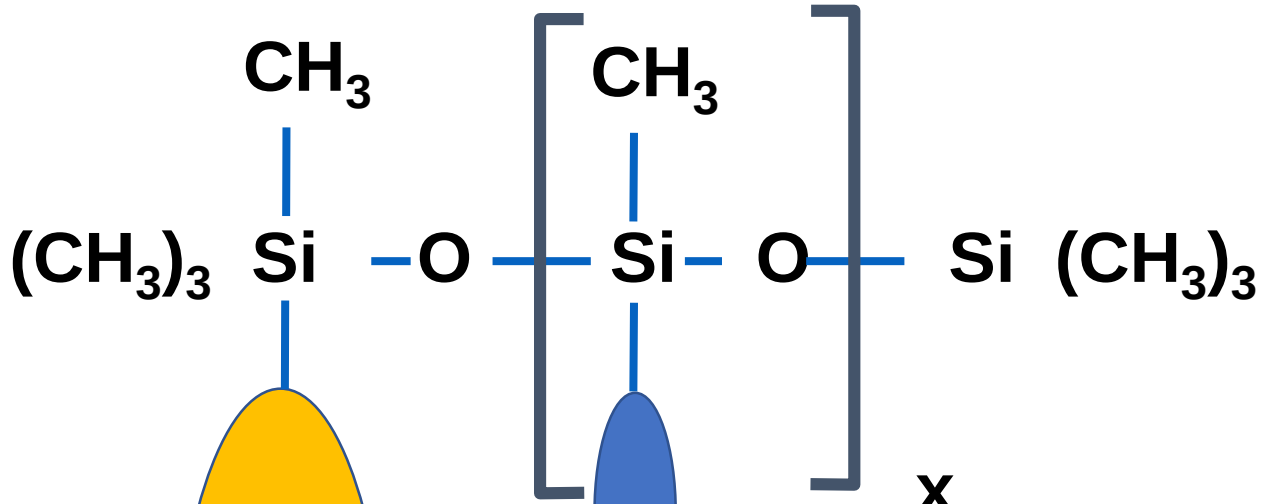
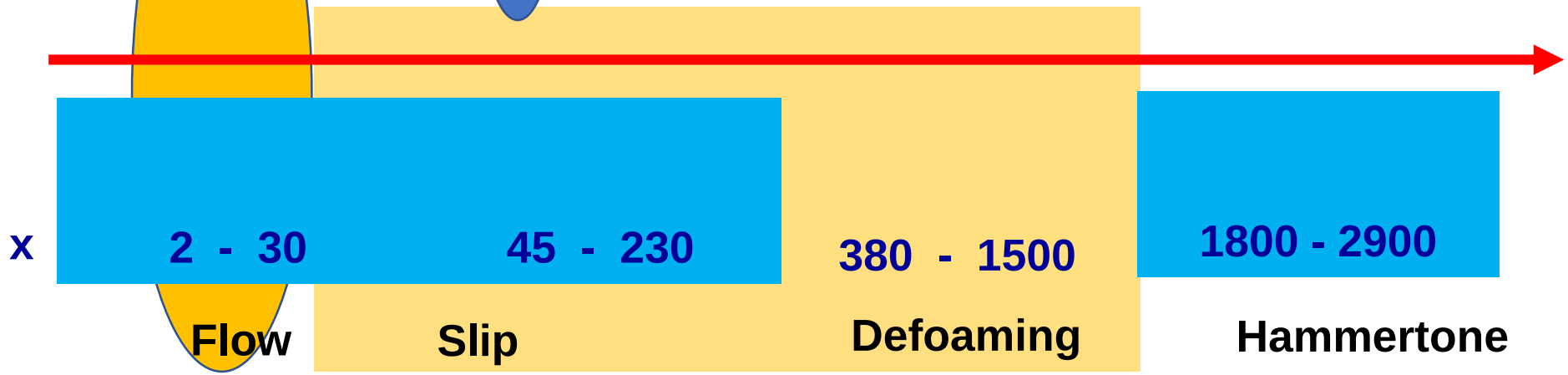
Compatibility

Polyether (EP/PO)
Aryl/alkyl
Polyester
Reactive Groups
-Acrylate
-COOH
-OH

PDMS

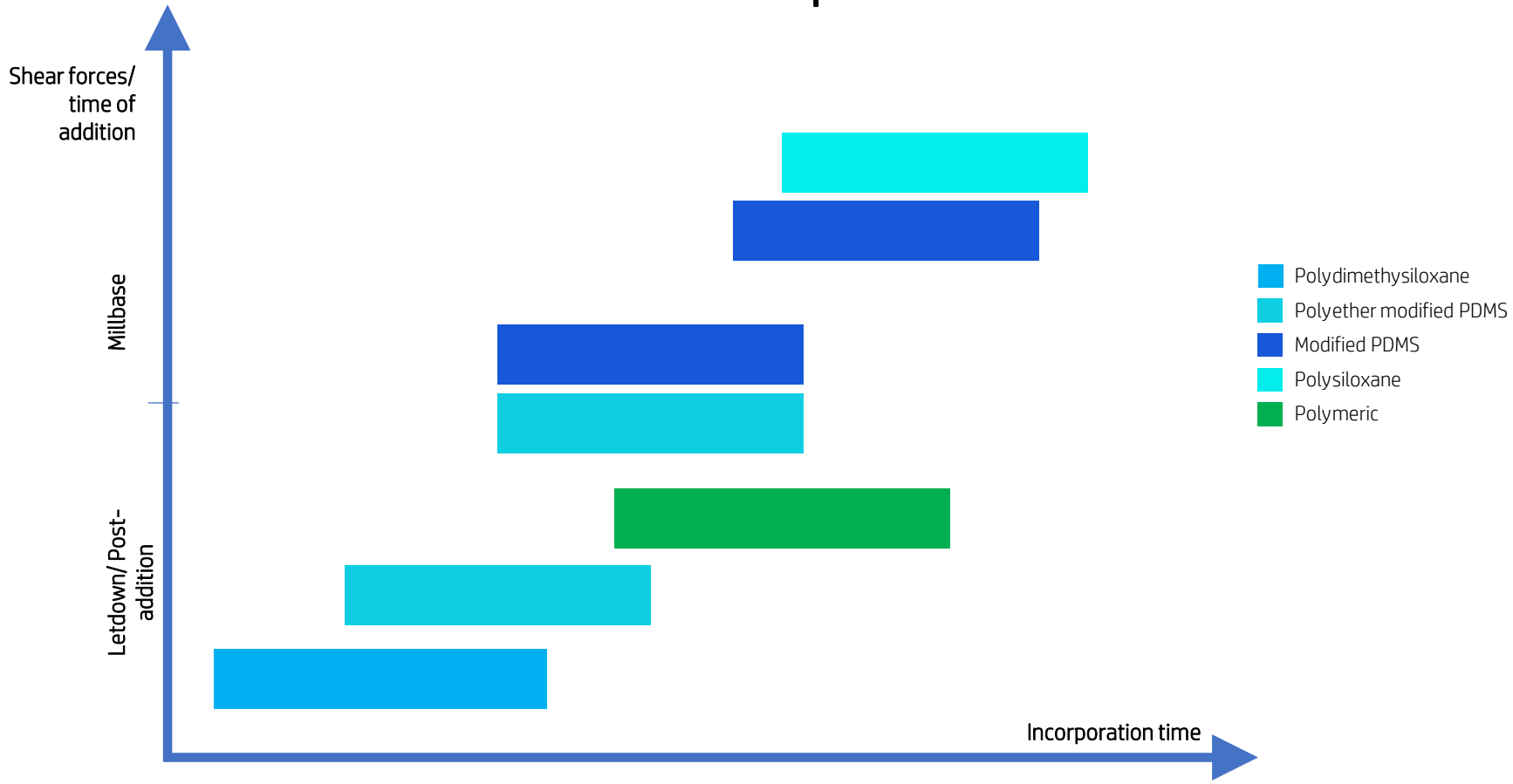


Modifications for range of surface effects; wetting, high to no slip, leveling &/or defoaming



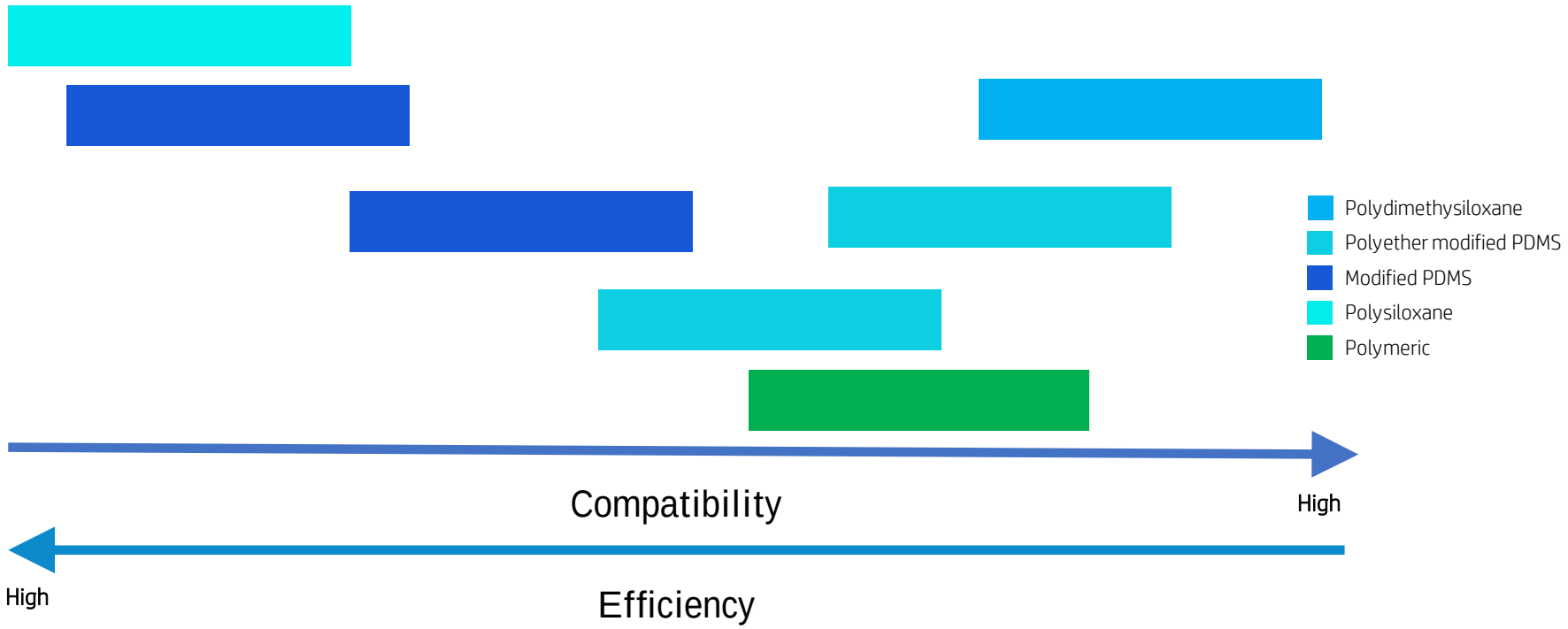
Polysiloxane and Polymeric defoamers

Selection of defoamers based on incorporation Shear



Polysiloxane and Polymeric defoamers

Selection of defoamers based compatibility and efficiency



Recommended Defoamer Selection

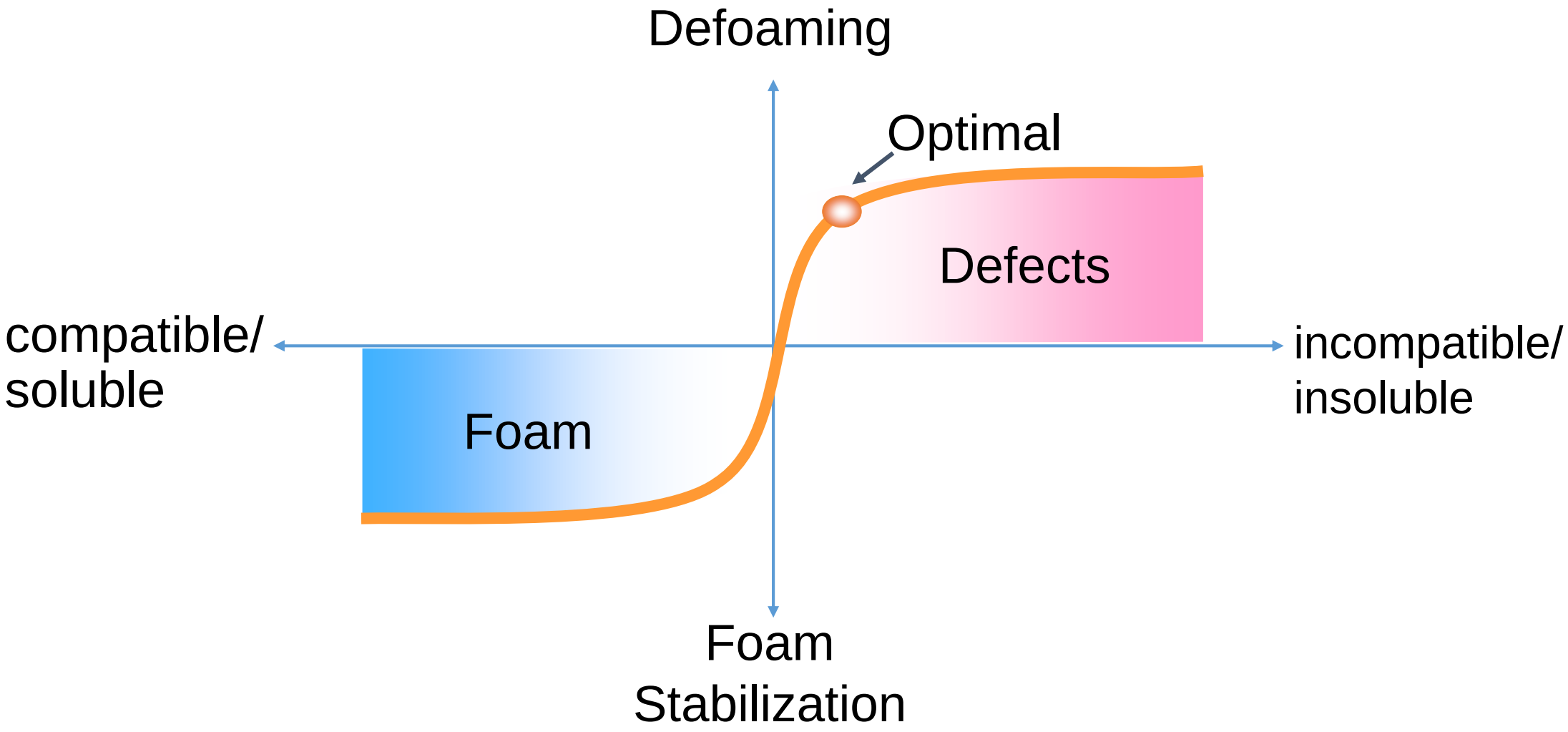
Replicate production shear for selection

Choose strongest defoamer that does not cause defects

Use a weaker defoamer for lower shear conditions

Confirm selection by testing multiple lots of RMs

Defoamer Selection



Defoaming vs Deaeration

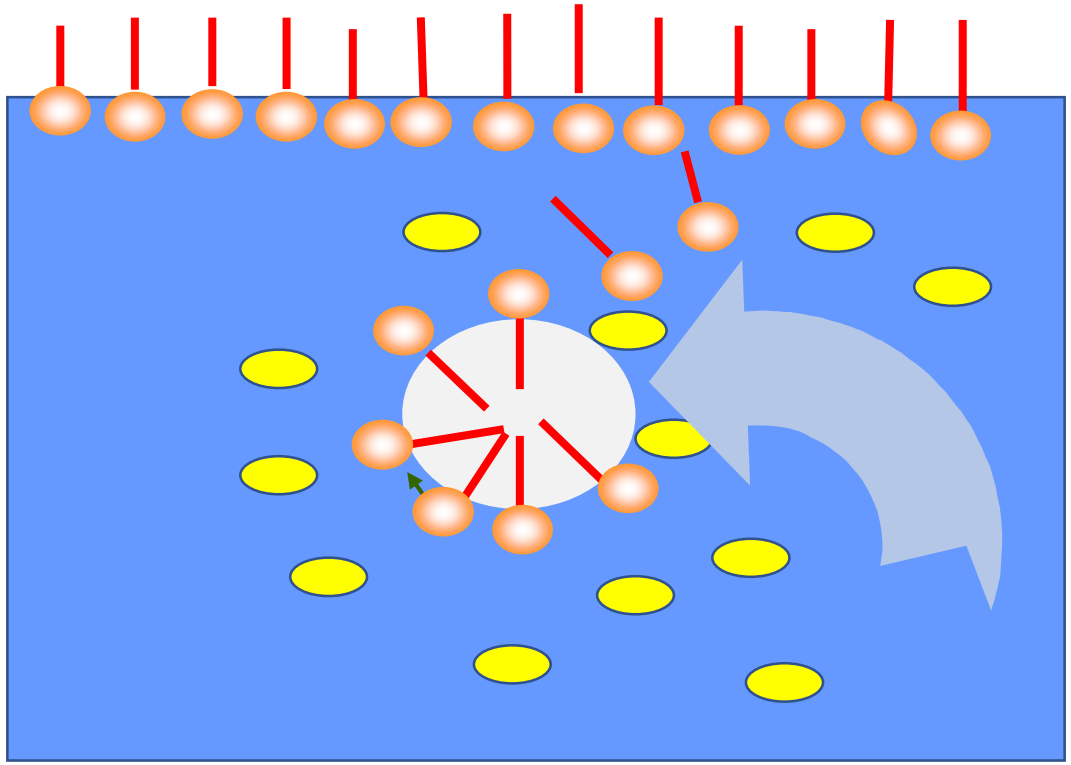
Defoamers destabilize the lamella of the bubbles at the surface of the liquid

Submerged bubbles have only one air liquid interface
Two small bubbles will coalesce to form a larger bubble of lower energy

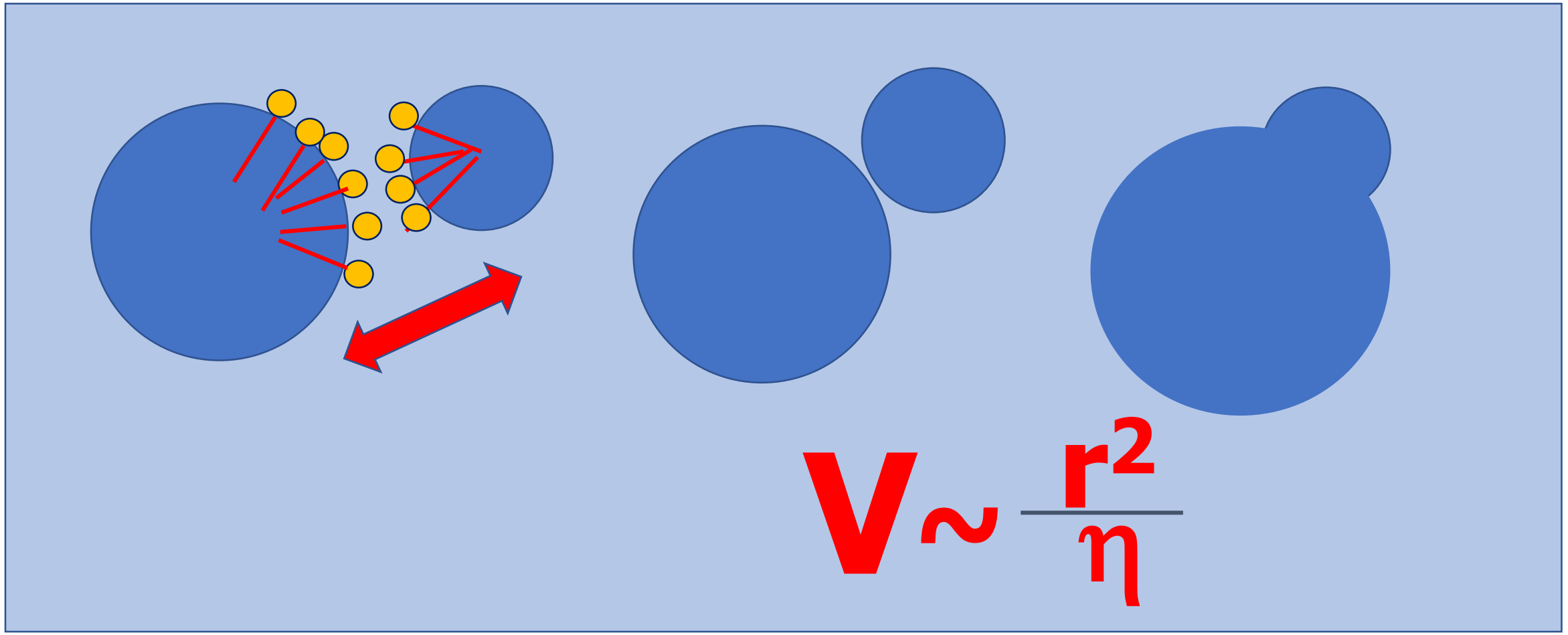
Two bubbles in contact have a lamella between them until coalescence
Removal of lamella stabilizing surfactants lowers bubble coalescence energy

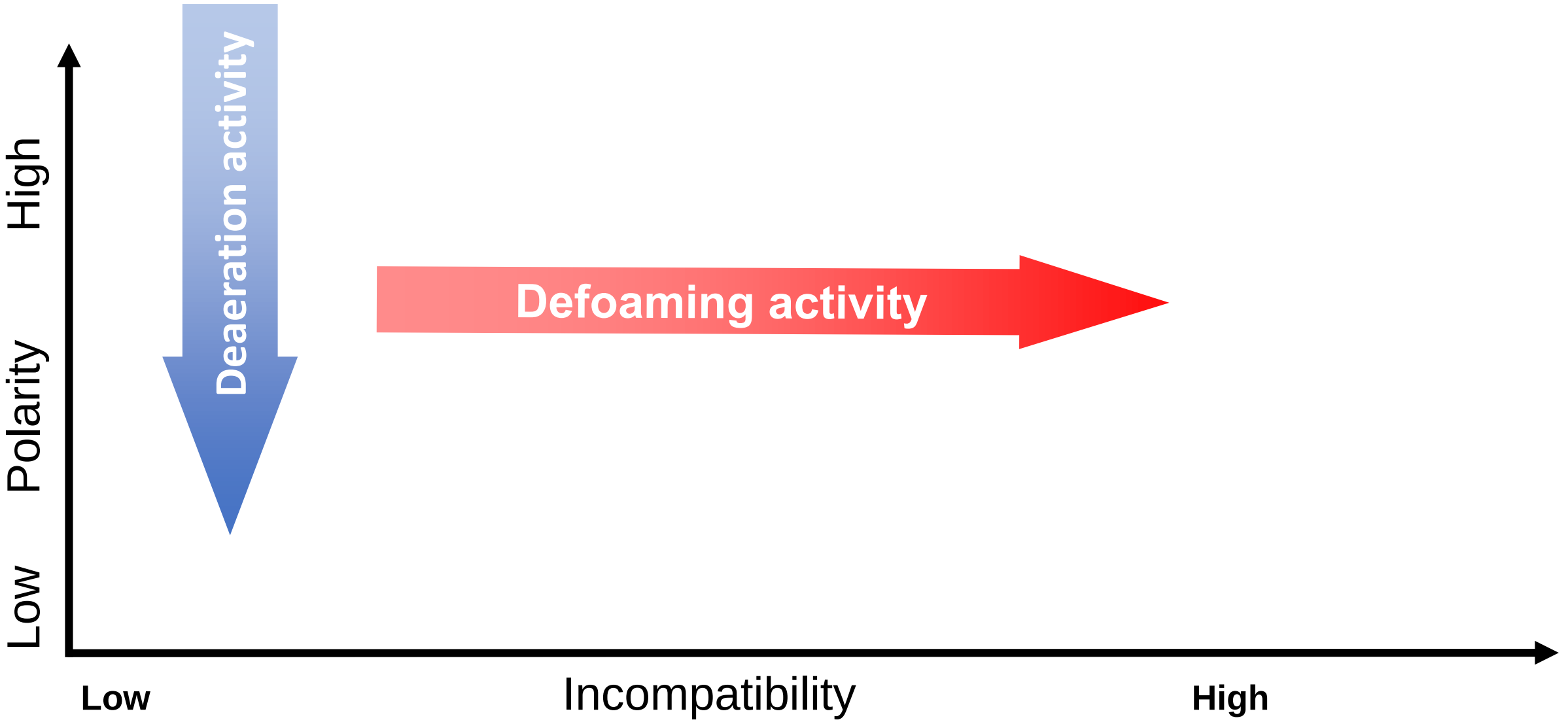
Deaerating agents are apolar species that lower bubble coalescence energy
They function to displace the lamella stabilizing surfactants

Deaeration - Mechanisms

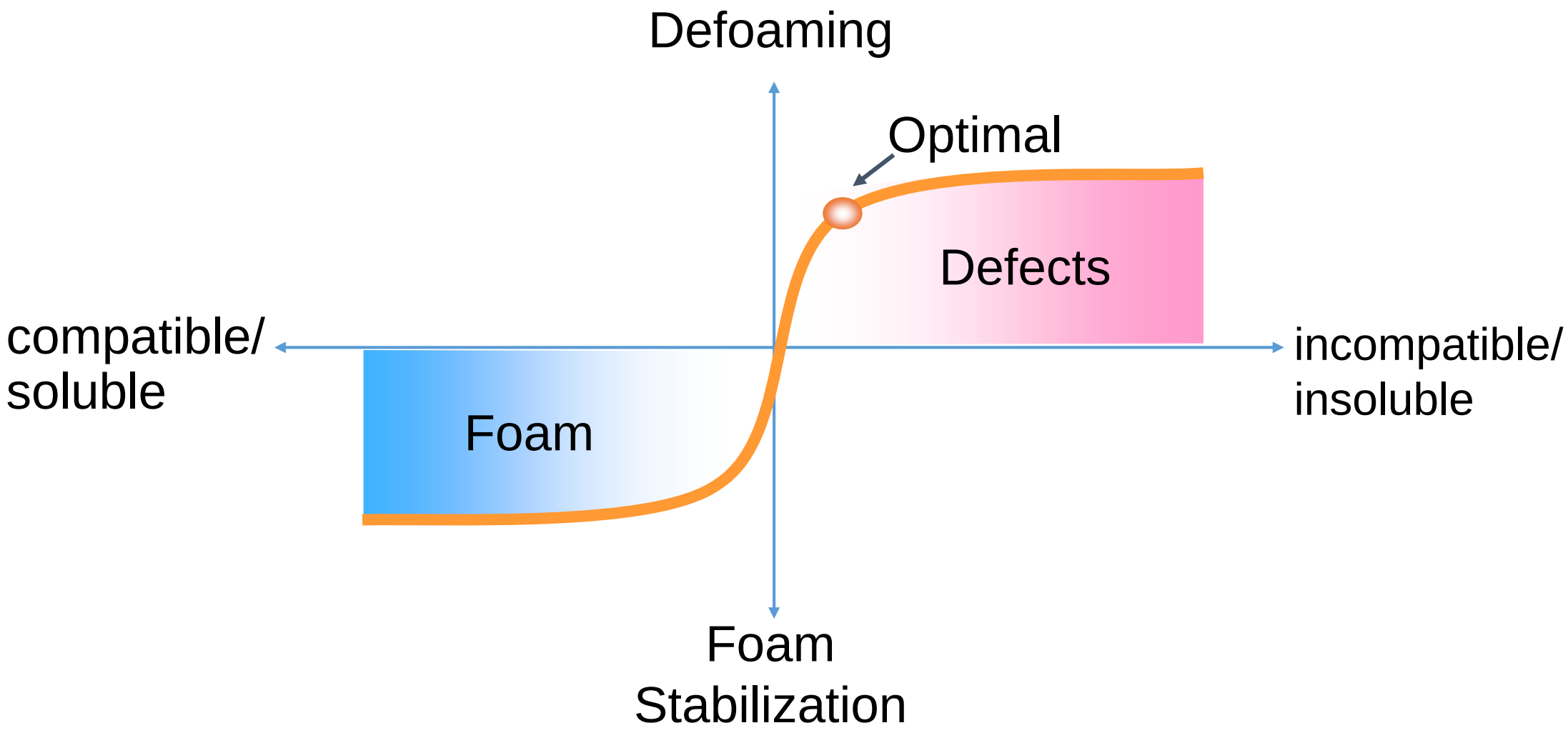


Lower polarity deaerating agents displace surfactants on bubble surface

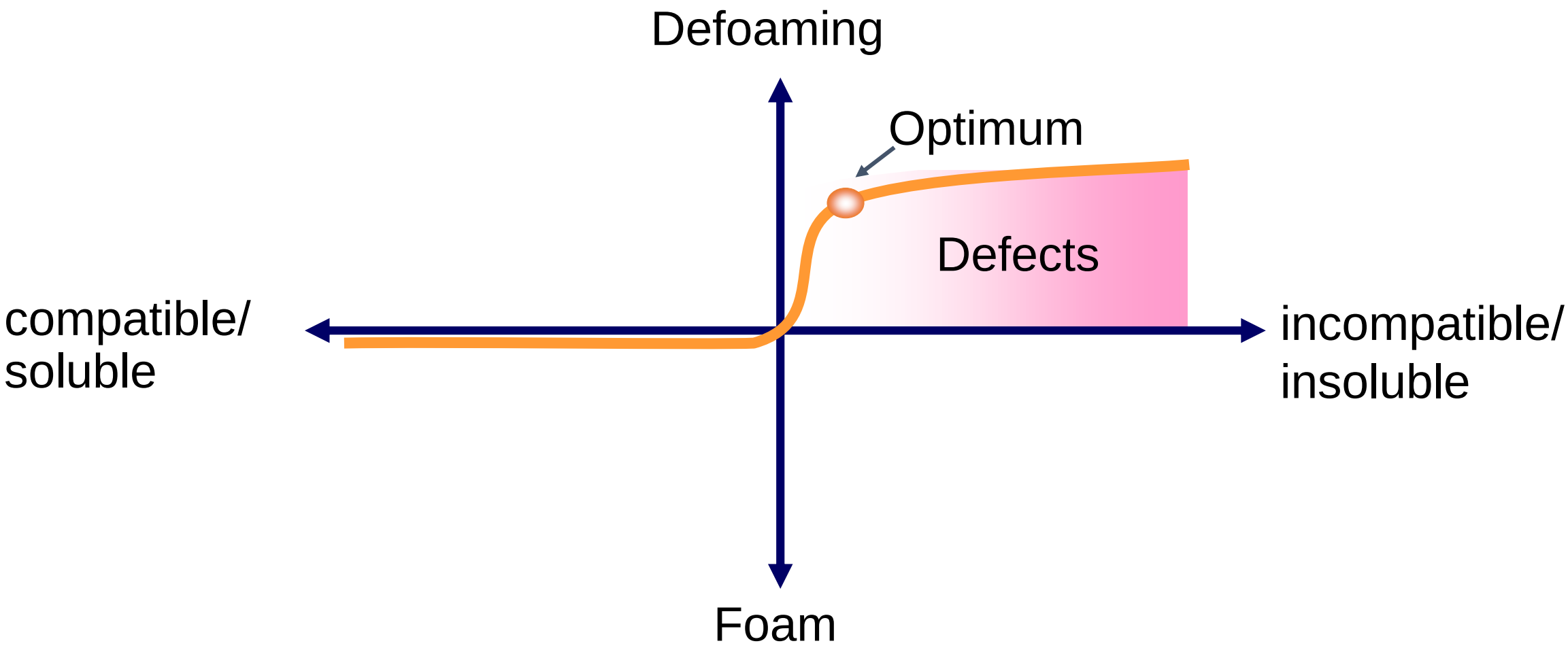

$V \sim \frac{r^2}{\eta}$


Deaeration activity
Defoaming activity
High
Polarity
Low
Low
Incompatibility
High

Defoamer


Defoaming
Optimal
Defects
compatible/
soluble
incompatible/
insoluble
Foam
Foam
Stabilization

Deaeration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Air/Liquid Interfaces in Organic Coatings

- Foam
- Bubbles or air entrapment
- Film surface

Flow & Leveling

- Flow is the movement of materials under shear (low)
  - Wetting, spreading, leveling, sagging
- Good flow does not guarantee leveling
  - Leveling is the formation of a smooth flat surface
  - Minimum surface area is a smooth flat surface
  - Texture or roughness increases surface area

Insufficient or Excessive Flow

- Surface Tension gradients (Bénard Cells)
- Rapid surface tension changes
- Poor or slow substrate wetting/penetration
- Non-optimal application conditions
- Non-optimal application equipment
- Porous substrate’s non-uniformity

Additive Location Determines Function

- Compatibility will locate additive in the bulk liquid
  - Wetting and Spreading
- Incompatibility will drive additive to liquid air interface
  - Surface modifying additive
  - Spreading, Slip, Defoaming, Leveling
- Extreme incompatibility will cause film defects
  - Haze, seeds, gloss loss, craters

Additives for affecting flow

- Surface tension modifying additives - Wetting Additives
  - Moderate to high solubility in continuous phase
  - Moderate to high mobility to migrate to newly created interfaces
  - Application creates new surfaces and interfaces rapidly
  - σ of liquid $\leq$ σ substrate for spontaneous wetting; contact $<$ = 0°
  - Material movement is always towards higher σ region

Additives for Leveling

- Controlled incompatibility concentrates the additive at the liquid coating/ air interface
- Too much compatibility will not show any leveling effect
- Too much incompatibility will cause film defects;

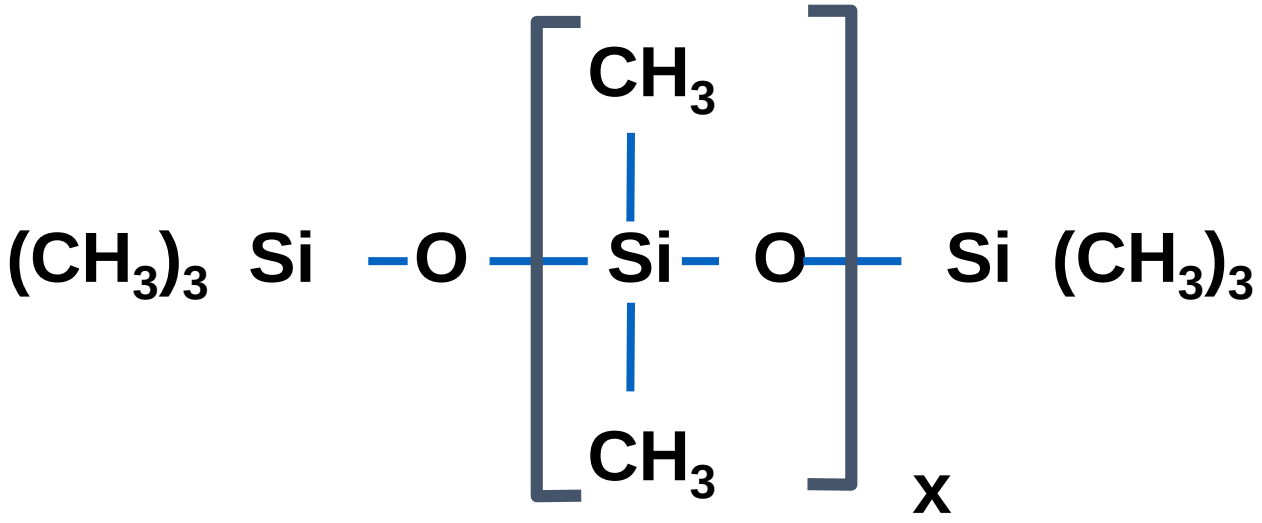
  haze, low gloss, seeds, craters

Surface Modifications by Controlled Incompatibility

Polymeric modifications for controlling balance of compatibility and incompatibility

PDMS alkyl chain length controls degree of surface activity

PDMS Unmodified



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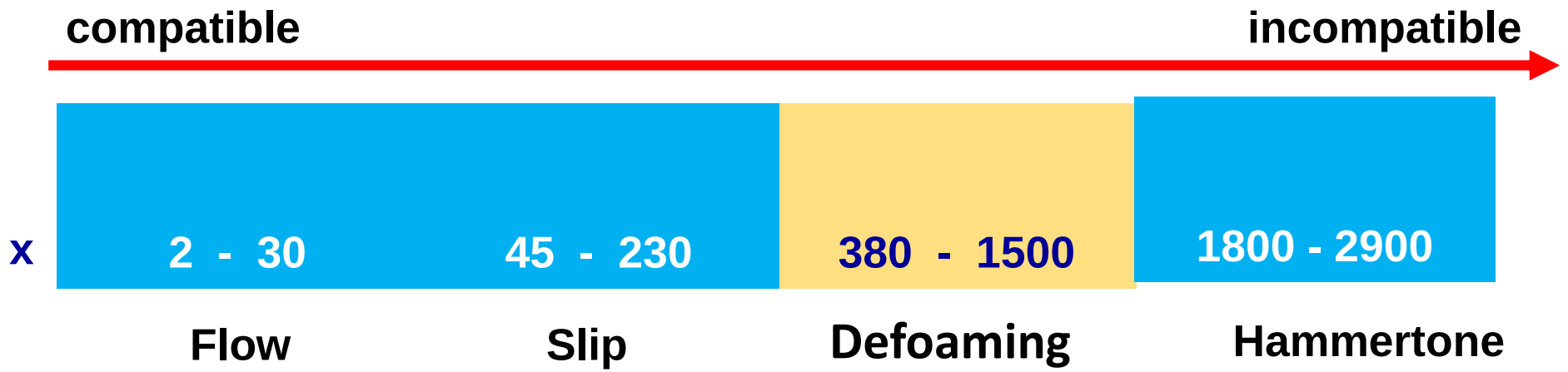

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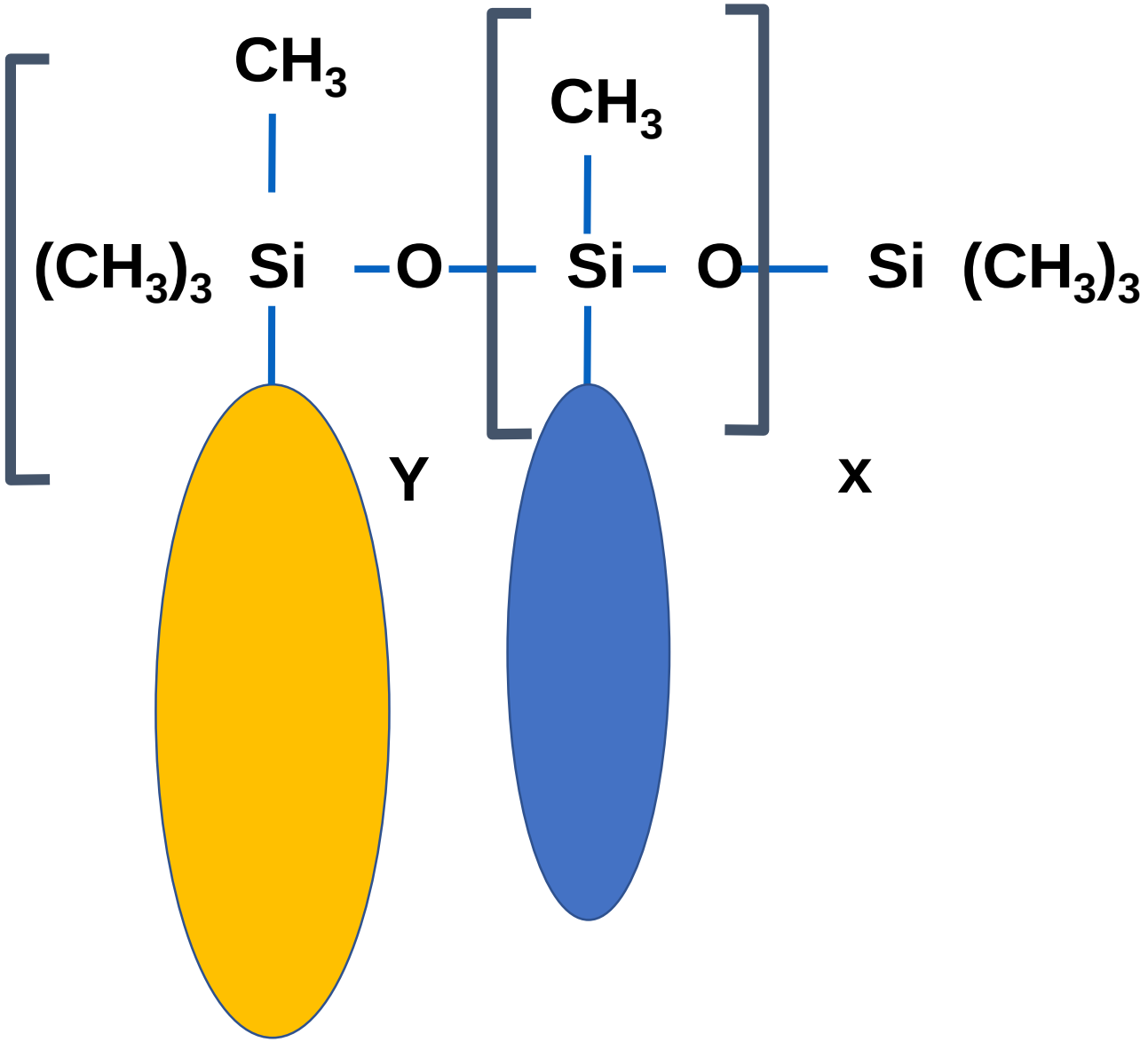

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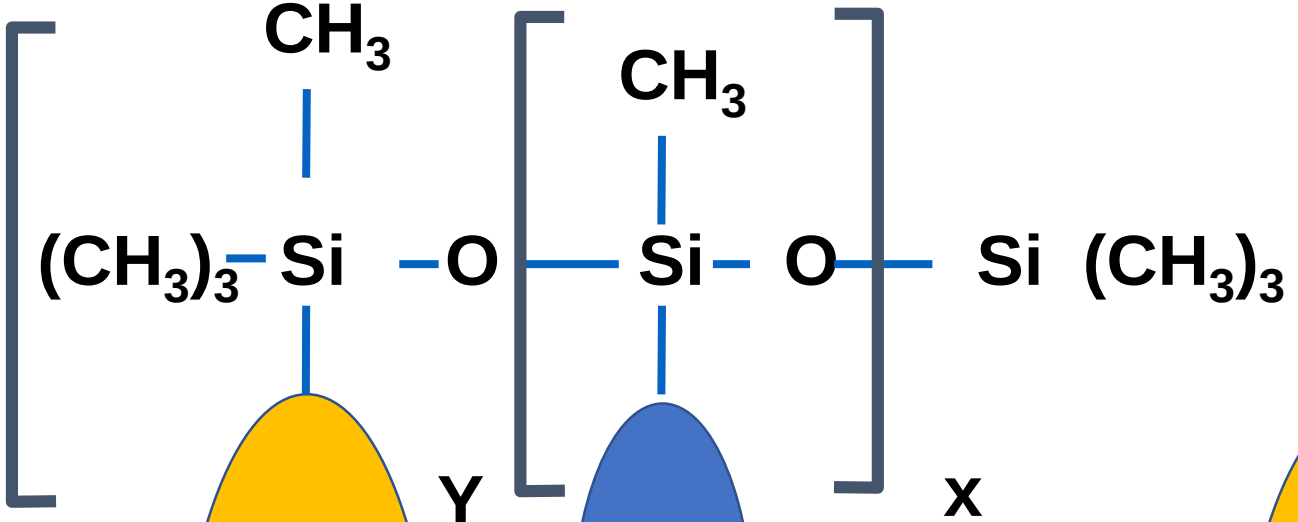

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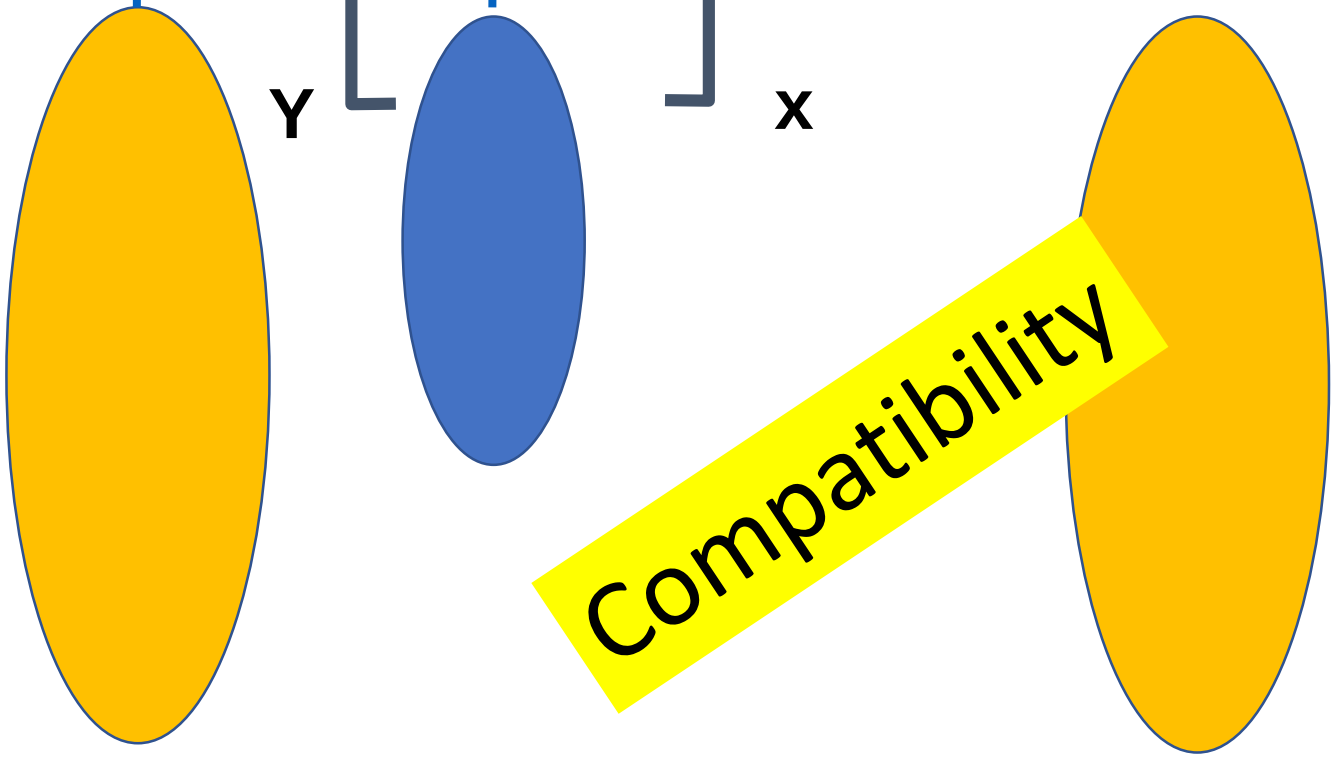

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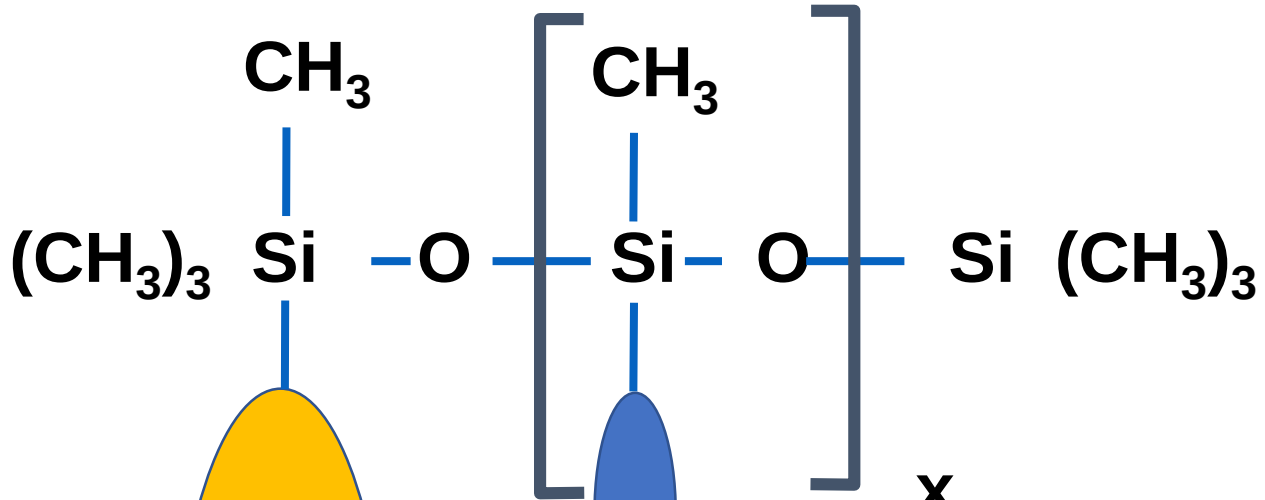


Modifications for range of surface effects; wetting, high to no slip, leveling &/or defoaming

Polymeric Leveling Additives

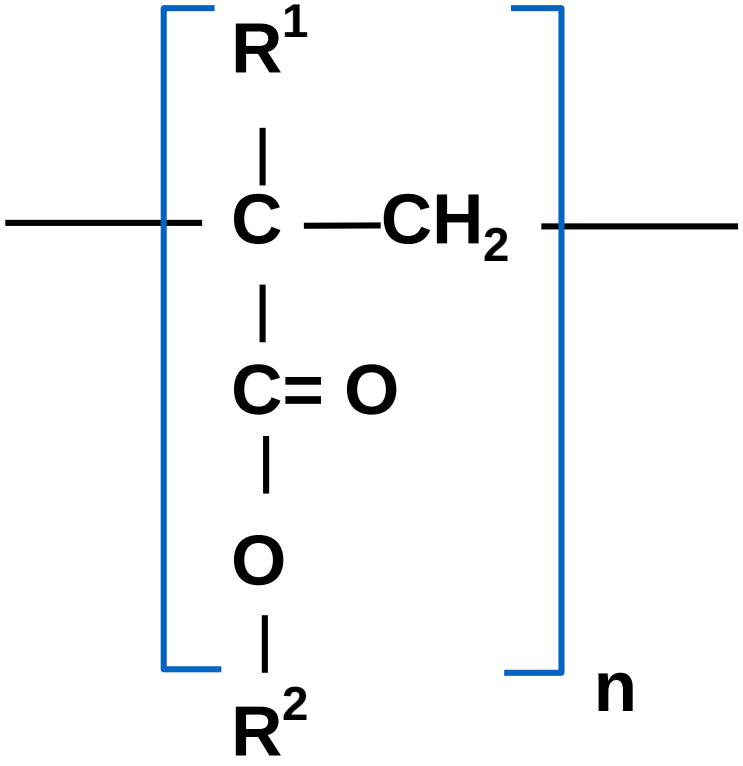
Effect

- minimal or no reduction of surface tension
- similar surface tension of film forming binders

Mechanism

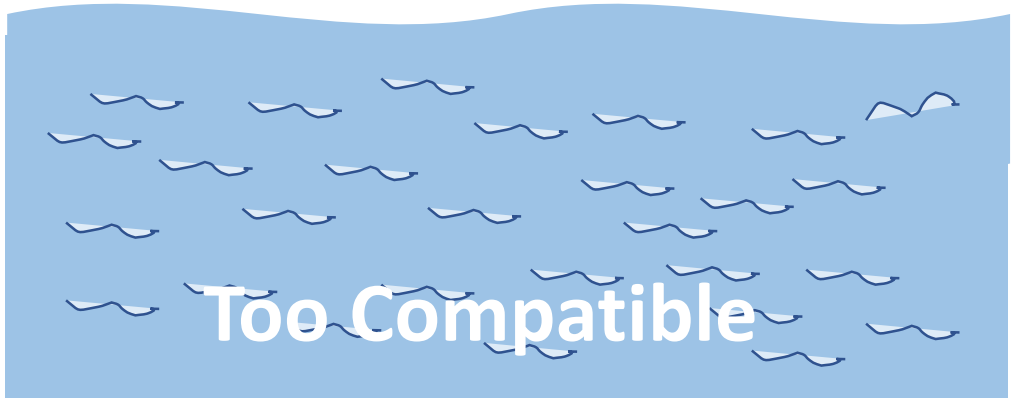
- controlled incompatibility by
  - variation of molecular weight
  - variation of compatibility with coating formulation

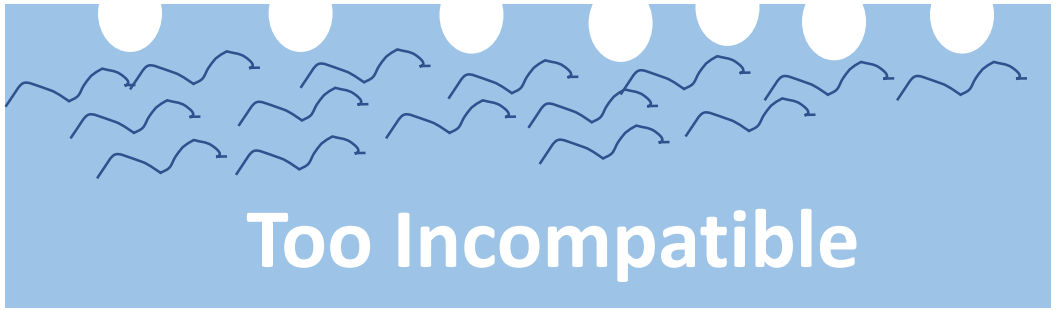
Chemistry of Polymerics



- homopolymers,
  statistical or block copolymers
- R^1 = - H (Acrylate)
  - CH_3 (Methacrylate)
- R^2 = - Alkyl
  - Polyester
  - Polyether
  - Salt
- possible - OH
  reactive groups: - COOH

Leveling Mechanism





Controlled Incompatibility

Additive Location Determines Function

- Compatibility will determine what interface additive impacts
- Solubility and compatibility will place it in the bulk
  - Wetting, spreading, penetration
- Incompatibility will drive additive to liquid air interface
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Importance of Controlled Incompatibility

Questions ?